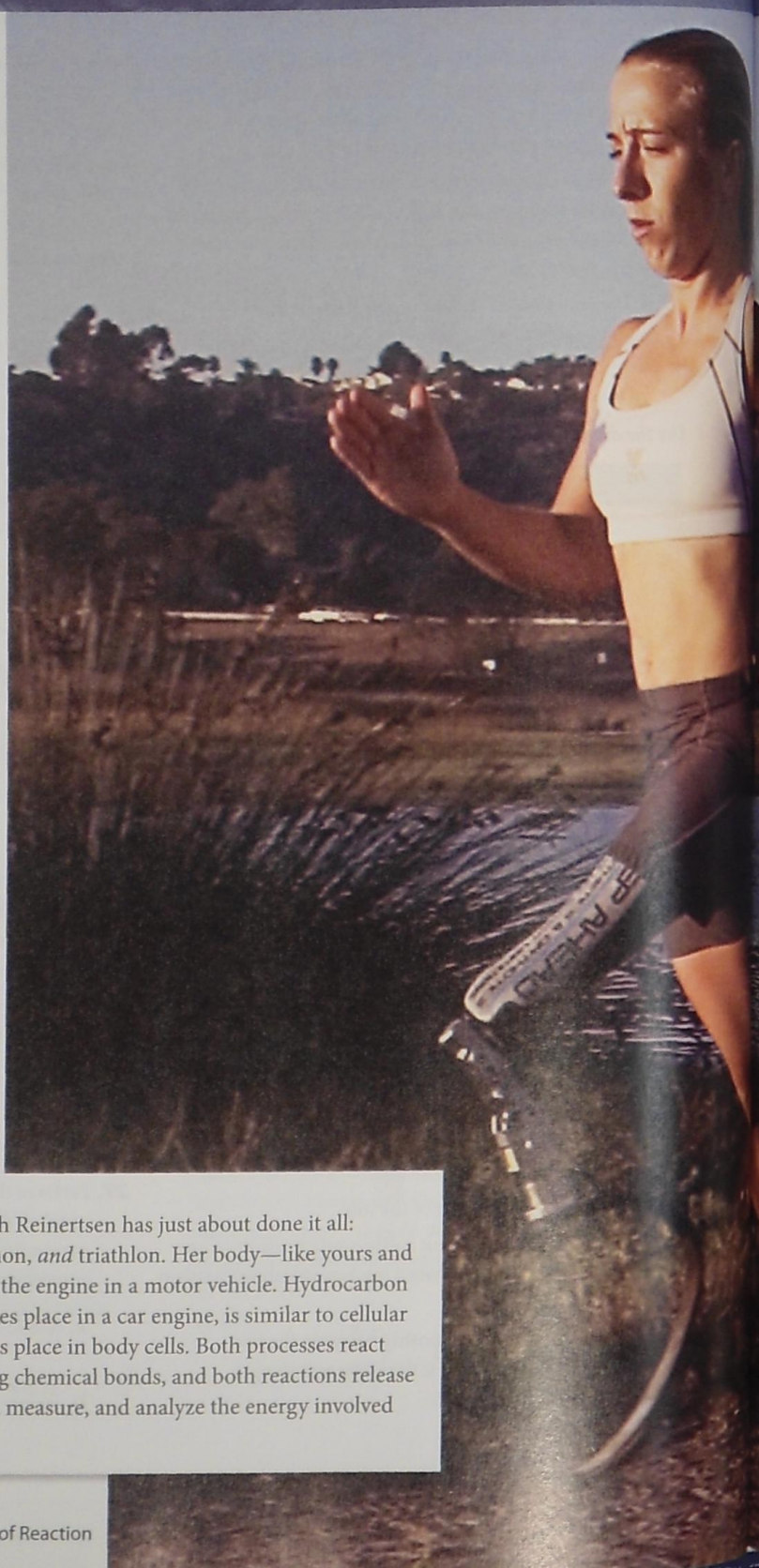


Specific Expectations

In this chapter, you will learn how to . . .

- D1.1 **analyze** conventional and alternative energy technologies, and **evaluate** their efficiency and environmental impact (5.4)
- D2.2 **write** thermochemical equations, expressing the energy change as a ΔH value or as a heat term in the equation (5.2, 5.3)
- D2.3 **solve** problems involving analysis of heat transfer, using $Q = mc\Delta T$ (5.1, 5.2, 5.3)
- D2.4 **plan** and **conduct** an inquiry to calculate, using a calorimeter, the heat of reaction of a substance, compare the actual heat of reaction to the theoretical value, and suggest sources of experimental error (5.2)
- D2.5 **solve** problems using Hess's law (5.3)
- D2.6 **conduct** an inquiry to test Hess's law (5.3)
- D2.7 **calculate** the heat of reaction for a formation reaction, using a table of standard enthalpies of formation and applying Hess's law (5.3)
- D3.1 **compare** energy changes from physical changes, chemical reactions, and nuclear reactions (5.1)
- D3.2 **compare** the energy change from a reaction in which bonds are formed with one in which bonds are broken, and **explain** them in terms of endothermic and exothermic reactions (5.1, 5.2, 5.3)
- D3.3 **explain** how mass, heat capacity, and change in temperature of a substance determine the amount of heat gained or lost (5.2, 5.3)
- D3.4 **state** Hess's law, and **explain** how it is applied to find the enthalpy changes of a reaction (5.3)

In the world of competitive running, Sarah Reinertsen has just about done it all: 100 m, 200 m, 400 m, 5 km, 10 km, marathon, *and* triathlon. Her body—like yours and everyone else's—has a lot in common with the engine in a motor vehicle. Hydrocarbon combustion, the chemical reaction that takes place in a car engine, is similar to cellular respiration, the chemical reaction that takes place in body cells. Both processes react “fuel” with oxygen by breaking and forming chemical bonds, and both reactions release energy. In this chapter, you will investigate, measure, and analyze the energy involved in chemical reactions.



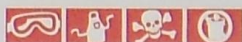
Launch Lab

Observing a Temperature Change

In a previous chemistry course, you may have heated a sample of copper(II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$, to drive off the waters of hydration. Here, you will react *anhydrous* $\text{CuSO}_4(\text{s})$ with water. In terms of energy, how does this reaction compare with the removal of the waters of hydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$?



Safety Precaution



- Do not inhale the anhydrous $\text{CuSO}_4(\text{s})$.
- Wear safety eyewear and protective clothing throughout this activity.
- Wash your hands thoroughly when you have completed this activity.

Materials

- 2 g of anhydrous $\text{CuSO}_4(\text{s})$
- 100 mL distilled water
- polystyrene cup
- 100 mL graduated cylinder
- stirring rod
- balance
- thermometer (alcohol or digital)

Procedure

1. Add approximately 100 mL of water to the cup.
2. Record the temperature of the water.
3. Add about 2 g of anhydrous CuSO_4 to the water. Stir the solution.
4. Record the highest temperature attained by the solution.
5. Dispose of the chemicals as instructed by your teacher when you have completed the activity.

Questions

1. Does this reaction absorb or release heat? How do you know?
2. What do you think the temperature change for this reaction would have been if only one half of the quantity of anhydrous $\text{CuSO}_4(\text{s})$ had been added to the same volume of water?
3. Given that energy has units of joules (J) and that temperature is measured in $^{\circ}\text{C}$ (or K), develop an equation that relates the energy (heat) obtained in this reaction to the observed temperature change, ΔT . (**Hint:** Recall what you learned about specific heat capacity in a previous science course.)

Key Terms

thermochemistry
open system
closed system
isolated system
thermal energy
temperature
specific heat capacity, c
first law of thermodynamics
enthalpy, H
endothermic
exothermic
second law of
thermodynamics
enthalpy of solution,
 $\Delta H_{\text{solution}}$

Figure 5.1 The chemical reaction that occurs when wood burns releases energy in various forms.



Whether they are chemical or physical, all changes in matter involve changes in the energy content of matter. Because energy-related technologies are so important to society, chemists and chemical engineers are especially interested in observing and measuring the amount of heat that is released during chemical and physical processes. In fact, an entire field of chemistry, called **thermochemistry**, is devoted to the study of heat involved in such changes. Over the next few pages, some foundational concepts for the study of thermochemistry are outlined. Several of these concepts, such as those associated with forms of energy, the transformation and transfer of energy, and the relationship between thermal energy and heat, are a brief review from previous science studies.

thermochemistry

the study of the energy changes involved in chemical and physical processes

Some Foundational Concepts for Thermochemistry

All forms of energy can be placed into one of two categories, kinetic energy and potential energy. Kinetic energy is the energy of motion. Anything that is moving has kinetic energy. Potential energy is the stored energy an object has as a result of its condition (for example, the nature of its particles in relation to one another—chemical potential energy) or its position (for example, its location above or below another object—gravitational potential energy).

The derived SI unit for energy is the joule (J), which is equivalent to a $\text{kg}\cdot\text{m}^2/\text{s}^2$. One joule is approximately the amount of energy necessary to lift one large kiwi (approximately 100 g) a distance of one metre. Since the amount of energy represented by a joule is very small, energy involving chemical reactions is often expressed in kilojoules ($1 \text{ kJ} = 1000 \text{ J}$).

System and Surroundings

Any sample under observation is referred to as a system. For example, the contents of the beaker in **Figure 5.2** can be considered to be a system. Everything that is not part of this system—that is, everything else in the entire universe—is considered the surroundings. These concepts can be expressed as an equation:

$$\text{universe} = \text{system} + \text{surroundings}$$

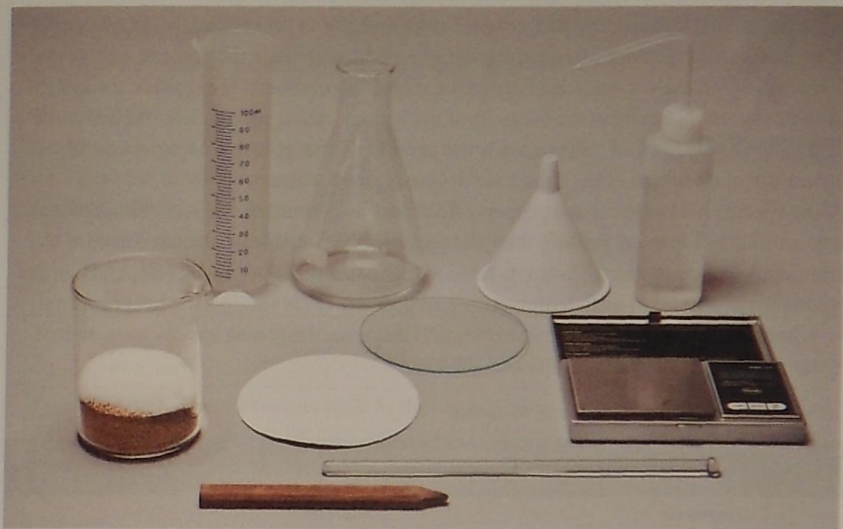


Figure 5.2 This photograph shows all the materials and equipment for a chemical analysis investigation. Once the contents of the beaker are defined as the system, everything else that is not the contents of the beaker become the surroundings. *Identify at least three other examples of surroundings in this photograph. (Count the equipment as a single item.)*

Usually, the parts of the surroundings that are relevant to the defined system are those that interact with it. Interactions between a system and its surroundings typically involve the exchange of energy and matter. Chemists have defined three types of systems with respect to such exchanges:

- An **open system** can exchange both energy and matter with its surroundings.
- A **closed system** can exchange energy, but not matter, with its surroundings.
- An **isolated system** cannot exchange energy or matter with its surroundings.

Figure 5.3 illustrates the three types of systems. An uncovered pot of potatoes boiling on the stove represents an open system. The system absorbs energy from the stove burner. The system loses both energy and matter when the water evaporates out of the pan in the form of steam. The pressure cooker with potatoes boiling on the stove represents a closed system because pressure cookers are sealed. The sealed lid prevents the loss of mass, or water in the form of steam, but heat can still enter the system through contact of the pot bottom with the stove. Finally, the pot of potatoes inside an insulated container represents an isolated system. The insulation prevents the exchange of any energy or matter between the system and its surroundings. It is difficult to completely isolate a system. Thus, some scientists claim that there is no truly isolated system except the universe itself.

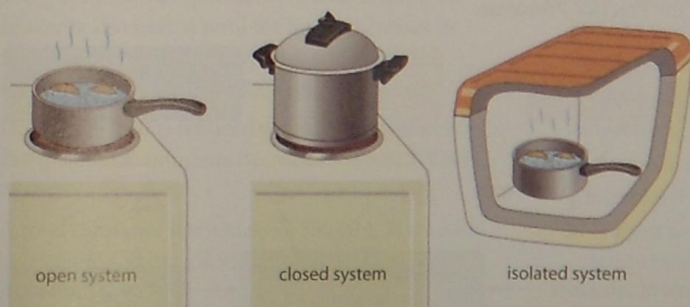


Figure 5.3 Comparing open, closed, and isolated systems.

Explain how the exchange of matter and energy is different in each situation.

open system a system that can exchange both matter and energy with the surroundings

closed system a system that can exchange only energy with the surroundings

isolated system a system that cannot exchange either energy or matter with the surroundings

thermal energy the sum of all the kinetic energies of all the particles of a sample of matter

temperature a measure of the average kinetic energy of all the particles of a sample of matter

specific heat capacity, c the amount of energy needed to increase the temperature of one gram of a substance by one degree Celsius

Measurable and Calculated Variables of a System

Certain properties of a system can be measured, and other properties cannot. For example, the **thermal energy** of a system—the sum of the kinetic energies of all the particles of the system—cannot be measured. However, you *can* measure the **temperature** of a system. The temperature of a system is directly related to the average kinetic energy of all of the particles of a system. You can also measure the volume of a system, the mass contained in a system, and the pressure that the system and surroundings exert on each other.

Measuring the temperature of a system before and after a process, such as a physical or chemical change, provides some of the data needed to calculate the amount of heat that has entered or left the system. Also needed for such a calculation is the mass of the system and an important property of the contents of the system, called specific heat capacity. The **specific heat capacity, c** , of a substance is the amount of energy needed to increase the temperature of one gram of the substance by one degree Celsius.

The specific heat capacity is a property that must be determined experimentally for every substance. Tables containing these data are readily available in print and online resources. A few examples are listed in **Table 5.1**. The specific heat capacity depends on the state of the substance. As well, temperature and pressure affect the specific heat capacity. The values in tables are usually reported for SATP, standard ambient temperature and pressure, which are defined as 25°C and 100 kPa.

Table 5.1 Specific Heat Capacities of Some Common Substances and Materials

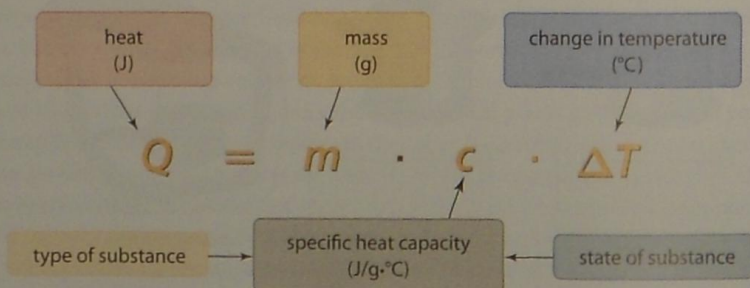
| Substance | Specific Heat Capacity (J/g·°C at SATP) | Substance | Specific Heat Capacity (J/g·°C at SATP) | Substance | Specific Heat Capacity (J/g·°C at SATP) |
|-------------------|---|------------------|---|-----------------|---|
| Elements | | Compounds | | Mixtures | |
| aluminum | 0.897 | Ammonia (liquid) | 4.70 | Air | 1.01 |
| carbon (graphite) | 0.709 | Ammonia (gas) | 2.06 | Concrete | 0.88 |
| copper | 0.385 | Ethanol | 2.44 | Glass | 0.84 |
| gold | 0.129 | Water (solid) | 2.00 | Granite | 0.79 |
| hydrogen (gas) | 14.304 | Water (liquid) | 4.19 | Wood | 1.26 |
| iron | 0.449 | Water (gas) | 2.02 | | |

Calculating the Amount of Heat Entering and Leaving a System

The amount of heat that enters or leaves an object when it is being heated or cooled can be calculated using the equation shown in **Figure 5.4**. The Greek letter delta, Δ , before the T represents a change in the temperature—that is, the final temperature minus the initial temperature: $\Delta T = T_{\text{final}} - T_{\text{initial}}$.

If ΔT is positive (if the final temperature is higher than the initial temperature), then Q is positive. A positive value for Q means that heat entered the system. If ΔT is negative, the initial temperature was higher than the final temperature, indicating that the temperature of the system decreased during the process. This would make Q negative, meaning that heat left the system. Practise using this formula by studying the following Sample Problem and completing the Practice Problems.

Figure 5.4 This equation enables you to calculate the amount of heat absorbed or released by a substance.



Sample Problem

Calculating the Absorption of Heat

Problem

When a 1.25 kg sample of water was heated in a kettle, its temperature increased from 16.4°C to 98.9°C. How much heat did the water absorb?

What Is Required?

You need to calculate the amount of heat absorbed by the water.

What Is Given?

You know the mass of water: $m = 1.25 \text{ kg}$

You know the initial temperature: $T_{\text{initial}} = 16.4^\circ\text{C}$

You know the final temperature: $T_{\text{final}} = 98.9^\circ\text{C}$

You have the specific heat capacity of liquid water from **Table 5.1**: $c = 4.19 \text{ J/g}\cdot^\circ\text{C}$

| Plan Your Strategy | Act on Your Strategy |
|---|--|
| Determine the change in temperature of the water. | $\Delta T = T_{\text{final}} - T_{\text{initial}}$ $= 98.9^\circ\text{C} - 16.4^\circ\text{C} = 82.5^\circ\text{C}$ |
| Determine the amount of heat absorbed by the water. Use the formula $Q = mc\Delta T$. Because the mass was given in kilograms, be sure to convert to grams, because the specific heat capacity includes grams. | $Q = mc\Delta T$ $= (1.25 \text{ kg}) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \left(4.19 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \right) (82.5^\circ\text{C})$ $= 4.32 \times 10^5 \text{ J}$ <p>The water absorbs 432 kJ of heat.</p> |

Check Your Solution

The solution has the correct number of significant digits. The units are correct.

Practice Problems

- How much heat must be added to a 36.2 g sample of iron to increase its temperature by 250.0°C?
- How much heat must be added to 128.6 g of steam at 126.0°C to increase its temperature to 189.5°C?
- A $1.00 \times 10^2 \text{ g}$ sample of ethanol at 25.0°C is heated until it reaches 50.0°C. How much thermal energy does the ethanol gain?
- Beaker A contains 50 g of liquid at room temperature. The beaker is heated until the liquid increases in temperature by 10°C. Beaker B contains 100 g of the same liquid at room temperature. The beaker is also heated until the liquid increases in temperature by 10°C. In which beaker does the liquid absorb more heat? Explain your answer.
- How much heat is released when the temperature of 789 g of liquid ammonia decreases from 82.7°C to 25.0°C?
- A solid substance has a mass of 250.00 g. It is cooled by 25.00°C and loses 4.937 kJ of heat. What is the specific heat capacity of the substance? Identify the substance using the values in **Table 5.1**.
- The specific heat capacity of a compound used in fireworks is 0.800 J/g·°C. If it takes $8.04 \times 10^3 \text{ J}$ to heat this material from 20.0°C to 925.0°C, what mass of compound was used?
- One litre of water at 1.00°C is warmed by the addition of 4.00 kJ of heat. What is the final temperature of the water? (1.00 L of water has a mass of 1.00 kg.)
- On a warm day, how much solar energy does a 3.982 kg piece of concrete absorb as heat if its temperature increases from 13.60°C to 14.50°C?
- You have samples of air and hydrogen gas at room temperature, both having a mass of 10.00 g.
 - Compare the change in temperature of these two samples if each gains 500.0 J of thermal energy.
 - Suggest a reason for the difference in the temperature changes.

The First Law of Thermodynamics: Energy Is Conserved

When a system absorbs energy, the surroundings release it. Similarly, when a system releases energy, the surroundings absorb it. This exchange or transfer of energy between a system and its surroundings can be in the form of heat, chemical energy, mechanical (kinetic) energy, or any other form of energy. In fact, energy is usually transformed from one form to another during an energy transfer. For example, the combustion of gasoline in a car engine releases forms of energy that include kinetic energy of the car's moving parts, chemical energy of the battery, electrical energy of the dashboard components, radiant energy of the headlights, and thermal energy that warms the parts of the car and areas within it. The sum of these forms of energy equals the change in energy between the reactants and products as the gasoline undergoes combustion.

In this example, as well as in all other situations involving energy transformations, energy is neither created nor destroyed; it is transformed from one type of energy to another or transferred from one object to another. You might recognize this idea from earlier studies as the *law of conservation of energy*, which is also the first law of thermodynamics. Essentially, the **first law of thermodynamics** states that the total energy of the universe is constant. In the form of an equation, the law is as follows:

$$E_{\text{universe}} = \text{constant}$$

You could also say that the change in the energy of the universe is zero:

$$\Delta E_{\text{universe}} = 0$$

Since, when defining a system, the surroundings consist of everything else in the universe you could also say that the system plus the surroundings equals the universe:

$$\text{universe} = \text{system} + \text{surroundings}$$

From this equation, the total energy of the universe is equal to the total energy of the system plus the total energy of the surroundings:

$$E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}}$$

Similarly, any change in the total energy of the universe must be equal to the change in the total energy of the system plus the change in the total energy of the surroundings. Since the change in the total energy of the universe is equal to zero, the following applies:

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

By re-arranging this equation, any change in the total energy of the system must be equal and opposite to the change in the total energy of the surroundings:

$$\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$$

In terms of practical situations such as warming soup on a stove, thawing ice, and any laboratory situation involving physical and chemical changes, the implications of the first law of thermodynamics are relatively straightforward: for any system that gains energy, the energy must come from the surroundings; conversely, if any system loses energy, that energy must enter the surroundings.

Enthalpy, H

To express thermochemical changes, chemists need a system variable that is not affected by the conditions under which the process occurs. One such variable is called the **enthalpy, H** , of the system. Enthalpy, sometimes called the *heat content* of the system, is defined as the total energy of the system plus the pressure times the volume, or $H = E + PV$. It is not possible to measure the total enthalpy of a system, but it is possible to measure the *change* in the enthalpy of a system.

The symbol for an enthalpy change is ΔH . The enthalpy change of a system depends only on the initial state (condition) and on the final state of the system and is represented

first law of thermodynamics a law stating that energy can be converted from one form to another but cannot be created or destroyed; can be represented as

$$E_{\text{system}} = -E_{\text{surroundings}}$$

enthalpy, H the total energy of the system plus the pressure times the volume, or

$$H = E + PV$$

as $\Delta H = \Delta E + \Delta(PV)$. For reactions of solids and liquids in solutions that take place in, for example, an open beaker in a laboratory, we assume that there is no change in pressure or volume. The work done by the reaction on the surroundings, which is represented by $\Delta(PV)$, is zero. The heat exchanged between the system and the surroundings is equal to the enthalpy change of the system ($\Delta H = \Delta E = Q$).

Note, however, that the enthalpy change at one pressure is different from the enthalpy change at another pressure, because the initial and final states of the system are different at different pressures. In thermochemistry, atmospheric pressure is usually chosen with enthalpy, because it is easy to achieve; also, the specific heat capacity of substances is reported for atmospheric pressure.

If heat enters the system during a process, the enthalpy change is positive, because the enthalpy of the system has increased. The process is said to be **endothermic**. If heat leaves a system during a process, the enthalpy change is negative, because the enthalpy of the system has decreased. The process is said to be **exothermic**.

The Second Law of Thermodynamics

All processes always result in some amount of energy that does not and cannot do useful work. This is the fundamental fact behind the **second law of thermodynamics**. There are many ways to state this law, but the result is always the same—no process is completely, 100 percent efficient. The statement of the second law of thermodynamics that is critical in thermochemical experiments is that, *when two objects are in thermal contact, heat is always transferred from the object at a higher temperature to the object at a lower temperature until the two objects are at the same temperature*.

Figure 5.5 illustrates the second law of thermodynamics. The length of the arrows represents the relative amount of kinetic energy of each particle. When a hot object and a cold object are separated by an insulator, their temperatures remain constant. When the objects are placed in thermal contact, the high-energy (hot) particles are able to collide with the low-energy (cold) particles. With each collision, the high-energy particle transfers some of its energy to the low-energy particle. Eventually, the energy is equally distributed among all the particles in the two systems. When two systems have reached the same temperature, they are in *thermal equilibrium*. (In fact, the particles have a range of energies, but their average energy is intermediate between that of the original hot and cold objects, and the particles with different energies are equally distributed throughout the combined systems.)

endothermic describes the process during which heat enters a system

exothermic describes the process during which heat leaves a system

second law of thermodynamics a law stating that when two objects are in thermal contact, heat is always transferred from the object at a higher temperature to the object at a lower temperature until the two objects are at the same temperature

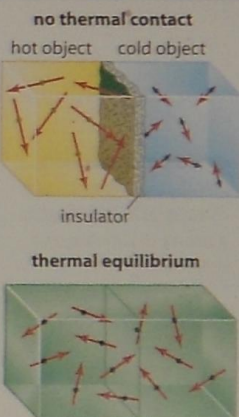


Figure 5.5 Two systems will eventually reach thermal equilibrium if they are in thermal contact.

Learning Check

- Describe three examples from daily life in which an object in thermal contact with another object can transfer heat to it.
- In what ways can a closed system exchange energy with its surroundings?
- Under what conditions does the enthalpy change of a system equal the heat exchanged between the system and the surroundings?
- The combustion of fuels in automobiles is an exothermic reaction. Thermal equilibrium is not achieved between the enthalpy of combustion from automobiles and the surroundings. Is this an exception to the second law of thermodynamics? Explain your answer.
- Explain the difference between an endothermic and an exothermic process.
- A compound such as calcium carbonate can decompose by absorbing energy. This reaction can be written as shown:

$$\text{CaCO}_3(\text{s}) + \text{energy} \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
 - Identify which has the greater potential energy: the reactants or the products.
 - Is the enthalpy of the system increasing or decreasing? Is the reaction endothermic or exothermic? Is the enthalpy change positive or negative?

Comparing Categories of Enthalpy Changes

Any type of process is accompanied by a change in the enthalpy of the system. There are three fundamental types of processes for which enthalpy changes are considered: physical changes, chemical changes, and nuclear changes.

Physical Changes

Recall that a physical change in a substance is a change in its condition that does not change its chemical properties. There are two physical changes in systems that are associated with significant changes in the enthalpy of a system. One such change occurs when one substance dissolves in another. The most common situation is the dissolving of a solid in water. The second commonly encountered physical change that is accompanied with a large enthalpy change is the phase change.

Enthalpy of Solution

Three steps, each involving an enthalpy change, must occur for a solute to become dissolved in water or in another solvent.

- Bonds between molecules or ions of a solute must be broken to make room for the solvent molecules.
- Bonds between solvent molecules must be broken to make room for the solute molecules.
- Bonds must form between the solvent molecules and solute molecules or ions. These bonds can be intermolecular bonds, ionic bonds, dipole-dipole bonds, or any other type of bond between molecules or ions.

An enthalpy change is associated with each of these processes. The sum of all of these enthalpy changes is called the **enthalpy of solution, $\Delta H_{\text{solution}}$** .

Enthalpies of solution can be endothermic or exothermic, depending on the nature of the solute and the solvent. Examples of each are shown in **Figure 5.6**. Note that in both processes, the enthalpies associated with separating both solute and solvent particles (ions or molecules), $\Delta H_{\text{solvent}}$ and ΔH_{solute} , are positive. Energy is always required to break bonds. The enthalpy associated with mixing solute and solvent particles, ΔH_{mix} , is negative. Energy is always released when bonds form. The factor that determines whether the overall process is endothermic or exothermic is the relative sizes of the enthalpy of mixing and the sum of the enthalpies of separating the particles, $\Delta H_{\text{solvent}} + \Delta H_{\text{solute}}$.

enthalpy of solution, $\Delta H_{\text{solution}}$ the enthalpy change associated with a solute dissolving in a solvent

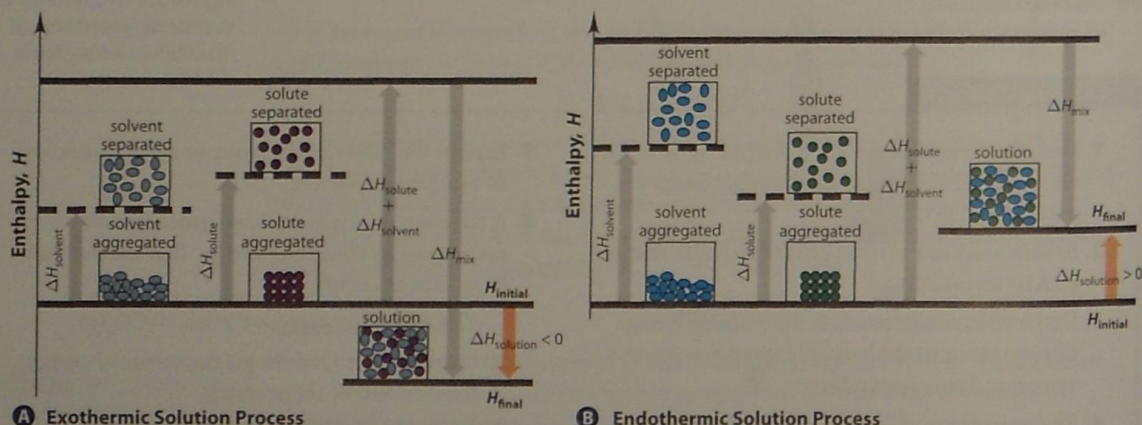


Figure 5.6 The three processes that occur when a substance is dissolved are represented here. Notice that $\Delta H_{\text{solvent}}$ and ΔH_{solute} are added together and placed in a single upward arrow in order to compare this sum with the ΔH_{mix} . The orange arrows show the size and direction of the arrow representing the overall enthalpy change for dissolving the substance. Enthalpies of solution can be exothermic (A) or endothermic (B).

Enthalpy of Phase Changes

In chemistry, a phase is any physically distinct, homogenous part of a system. The physical state of a substance—whether it is a solid, liquid, or gas—is an example of a phase. Phase changes are physical changes for which the enthalpy change is well-defined and thus can be easily studied.

A significant amount of heat must be added to or removed from a substance to change its phase. **Figure 5.7** defines the symbols for enthalpy changes that accompany phase changes. Subscripts are added to the symbol, ΔH , to identify the type of phase change. The superscripted symbol “o” is called “nought,” and it represents standard conditions. Because enthalpy changes vary with pressure, the values are reported for standard atmospheric pressure. The four phase changes represented in **Figure 5.7** are summarized below.

- Energy needed to change a solid into a liquid is called *enthalpy of melting* and is symbolized $\Delta H_{\text{melt}}^{\circ}$.
- Energy needed to change a liquid into a gas is called *enthalpy of vaporization* and is symbolized $\Delta H_{\text{vap}}^{\circ}$.
- Energy released when a gas becomes a liquid is called *enthalpy of condensation* and is symbolized $\Delta H_{\text{cond}}^{\circ}$.
- Energy released when a liquid becomes a solid is called *enthalpy of freezing* and is symbolized $\Delta H_{\text{fre}}^{\circ}$.

Notice that the magnitudes of $\Delta H_{\text{melt}}^{\circ}$ and $\Delta H_{\text{fre}}^{\circ}$ are equal, but the directions are opposite. Therefore, one phase change is the negative of the other. The same is true for $\Delta H_{\text{vap}}^{\circ}$ and $\Delta H_{\text{cond}}^{\circ}$:

$$\Delta H_{\text{melt}}^{\circ} = -\Delta H_{\text{fre}}^{\circ}$$

$$\Delta H_{\text{vap}}^{\circ} = -\Delta H_{\text{cond}}^{\circ}$$

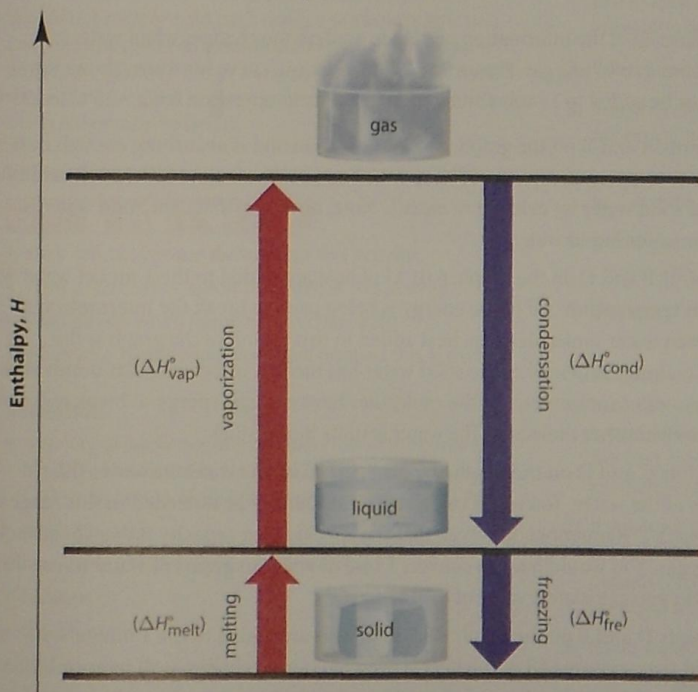


Figure 5.7 Enthalpy changes that accompany melting, vaporization, condensation, and freezing.

Terminology Differences with Enthalpy

The terminology used to describe enthalpy changes differs among textbooks and other information resources, so it is helpful to be aware of the other terms. Many resources use the term “heat” instead of “enthalpy.” For example, the enthalpy of vaporization is sometimes called the heat of vaporization. In older textbooks, it is called the latent heat of vaporization. As well, most advanced chemistry textbooks use only two symbols: one for the transition between a solid and a liquid and another for the transition between a liquid and a gas. The symbol $\Delta H_{\text{vap}}^{\circ}$ is used for both vaporization and condensation. You just use the positive value for vaporization and the negative value for condensation. Similarly, both $\Delta H_{\text{melt}}^{\circ}$ and $\Delta H_{\text{frc}}^{\circ}$ are symbolized $\Delta H_{\text{fus}}^{\circ}$ and called the enthalpy of fusion.

Enthalpy and the Heating Curve of Water

Table 5.2 lists enthalpies of melting and vaporization for selected substances. Enthalpies for phase changes are typically reported in kilojoules per mole, kJ/mol.

Table 5.2 Enthalpies of Melting and Vaporization for Selected Elements and Compounds

| Substance | $\Delta H_{\text{melt}}^{\circ}$ (kJ/mol) | $\Delta H_{\text{vap}}^{\circ}$ (kJ/mol) |
|--------------|---|--|
| Water | 6.01 | 40.7 |
| Mercury | 2.30 | 19.2 |
| Oxygen | 0.44 | 6.82 |
| Methane | 0.94 | 8.19 |
| Acetic acid | 11.7 | 23.7 |
| Ethoxyethane | 7.19 | 26.5 |

You now have all of the information needed to analyze the changes when water is transformed from a solid to a gas. **Figure 5.8**, called a heating curve for water, shows how much heat must be added to 1 mol of water to increase its temperature from -25°C to 125°C .

- Between points A and B on the graph, the water is solid and is absorbing enough heat to increase the temperature from -25°C to 0°C . You could calculate the amount of heat added to the solid water by using $Q = mc\Delta T$. Note, however, that c for solid water is different from c for liquid water.
- Between points B and C on the graph, 6.01 kJ of heat are added to the 1 mol of water with no change in temperature. All of the energy is being used to break the intermolecular bonds between water molecules. The heat added in this region of the graph is the enthalpy of melting. When all of the solid water has melted, intermolecular bonds still exist between water molecules, but the molecules have enough energy to break away and then bond with another molecule. The water is in its liquid state.
- Between points C and D on the graph, the heat gained by the water increases the temperature of the water. You could calculate the amount of heat needed in this range by using $Q = mc\Delta T$. Remember, however, that the specific heat capacity is usually given in joules per gram. You would have to convert 1 mol of water to grams of water to use the formula. (Did you calculate a value of 8.18 kJ for Q ?)
- Between points D and E on the graph, 40.7 kJ of heat are added to the 1 mol of water with no change in temperature. All of the heat is used to completely break all intermolecular bonds between water molecules and allow the molecules to escape from the liquid. This amount of heat is equal to the enthalpy of vaporization.
- Finally, between points E and F on the graph, the heat that is added to the water increases the temperature of the gaseous water. Once again, you could calculate this amount of heat by using $Q = mc\Delta T$, where c is the specific heat capacity of gaseous water.

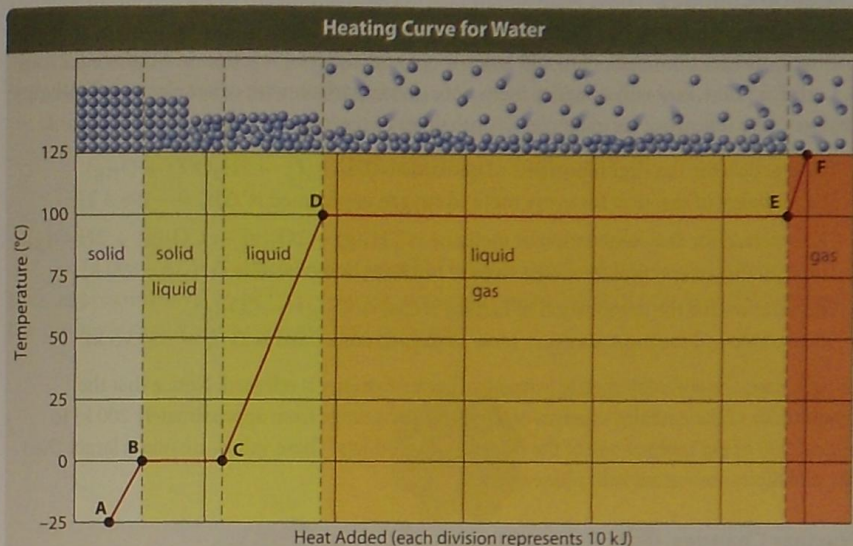


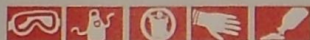
Figure 5.8 The illustrations above this heating curve for water represent water molecules as they interact with one another in different states and in transition between states.

Activity 5.1

Make Your Own Hot Pack or Cold Pack

Commercially available hot and cold packs are useful for first-aid treatment when hot water or ice is not readily available. Also, hot packs are used by hikers and mountaineers in cases of extreme cold. You can make a simple hot pack or cold pack using a sealable plastic bag containing a solid compound, usually ionic. When water is added, the reaction either absorbs heat or gives off heat. In this activity, you will prepare either a hot pack or a cold pack using only these materials.

Safety Precautions



- Wear safety eyewear throughout this activity.
- Wear a lab coat or apron throughout this activity.
- Wear gloves when handling the chemicals.
- Wash your hands when you have finished this activity.

Materials

- a variety of water-soluble compounds—for example, NH_4NO_3 , NH_4Cl , CaCl_2 , NaCl , NaCH_3CO_2 (anhydrous), CaO (anhydrous), MgSO_4 (anhydrous), urea (H_2NCONH_2)
- distilled water
- resealable plastic bags (small and large)
- balance
- thermometer
- 100 mL graduated cylinder
- 100 mL beaker

Procedure

1. With your group, devise an initial design for your hot pack or cold pack that will allow you to quantitatively test at least one compound for its effectiveness at absorbing or releasing heat.
2. Construct a data table to record appropriate data.
3. Test your design with one of the available compounds. If necessary, refine your design.
4. Using your refined design, test one of the compounds for its suitability as a hot pack or a cold pack.
5. If time permits, repeat this investigation using another compound.
6. Dispose of the waste as directed by your teacher.

Questions

1. Based on your data or class data, which compound would make the best hot pack? Why? Which would make the best cold pack? Why? Use the terms *endothermic* or *exothermic*, and *system* and *surroundings* in your answers.
2. If you were to prepare a hot pack or a cold pack for commercial use, what safety concerns should you consider? Explain how you could use material safety data sheets to obtain safety information.
3. If you were to prepare these hot packs or cold packs commercially, what design changes would you like to make?
4. What economic factors would you take into account before preparing a commercial hot pack or cold pack?

Chemical Changes

Every chemical reaction has an enthalpy change associated with it. The symbol for the enthalpy of reaction is ΔH_r . You will learn about enthalpies of reaction in Sections 5.2 and 5.3. At this point, you will consider them only in comparison with other classes of enthalpy changes. The following are examples of enthalpies of reaction for a few simple reactions.

- The reaction for the decomposition of peroxide is $2\text{H}_2\text{O}_2(\ell) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$.
The enthalpy of reaction for every mole of oxygen gas formed is $\Delta H_r = -196.4 \text{ kJ}$.
- The reaction for the combustion of methane is $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$.
The enthalpy of reaction for every mole of methane combusted is $\Delta H_r = -890 \text{ kJ}$.
- The reaction for the combustion of carbon is $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$.
The enthalpy of reaction for every mole of oxygen consumed is $\Delta H_r = -393.5 \text{ kJ}$.

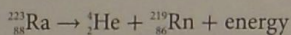
In each case, the enthalpy change is negative because energy is released. Notice that the magnitudes of the enthalpy changes of these reactions range from approximately 200 kJ to almost 900 kJ per mole of one of the reactants or products. These values are much larger than the enthalpies associated with phase changes.

Nuclear Changes

Atoms of some elements spontaneously emit particles from their nuclei and are transformed into other elements. Two different particles can be emitted. The nuclei of some radioactive isotopes emit beta (β) particles, which are identical to electrons. The nuclei of other radioactive elements emit alpha (α) particles, which are identical to helium nuclei (two protons and two neutrons). As well, the total mass of the products is measurably smaller than the mass of the original nucleus. The missing mass is converted into energy according to Einstein's equation, $E = mc^2$, where m is the amount of mass that was converted into energy and c is the speed of light.

Alpha Decay

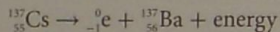
When a nucleus emits an α particle, the resulting nucleus has two fewer protons and two fewer neutrons. Therefore, its mass number is reduced by 4 and its atomic number is reduced by 2. For example, radium-223 emits an α particle and becomes a radon-219 atom. The nuclear reaction can be written as shown here, where the α particle is written as a helium atom.



When 1 mol of radium-223 decays into radon-219, $5.64 \times 10^8 \text{ kJ}$ of energy is released.

Beta Decay

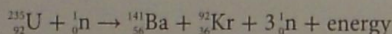
When a nucleus emits a β particle, a neutron in the nucleus becomes a proton. Therefore, the new nucleus has one less neutron and one more proton. For example, cesium-137 emits a β particle and becomes barium-137. This nuclear reaction can be written as shown below, where the β particle is written as an electron.



When 1 mol of cesium-137 decays into barium-137, $1.13 \times 10^8 \text{ kJ}$ of energy is released.

Nuclear Fission

Nuclear fission is a process in which a heavier nucleus is split into smaller, lighter nuclei with the release of energy. For example, bombarding uranium-235 with neutrons causes the uranium-235 nucleus to split into two smaller nuclei. The two smaller nuclei can vary among many combinations of elements. One example is shown as an equation below and it is also shown in **Figure 5.9**.



The sum of the masses of the products is 0.215 u (atomic mass units) or 3.57×10^{-28} kg less than the mass of a uranium atom. When 1 mol of uranium-235 fissions, the amount of mass that is converted into energy is 2.15×10^{-4} kg. You can calculate the amount of energy released when 1 mol of uranium-235 fissions, using $E = mc^2$ as shown below.

$$\begin{aligned} E &= mc^2 \\ &= (2.15 \times 10^{-4} \text{ kg}) \left(3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)^2 \\ &= 1.93 \times 10^{13} \text{ J} \end{aligned}$$

(Note: The unit $\text{kg} \cdot \text{m}^2/\text{s}^2$ is equivalent to the J.)

Thus, approximately 2×10^{10} kJ of energy is released when 1 mol of uranium-235 fissions. The products of nuclear fission are very radioactive.

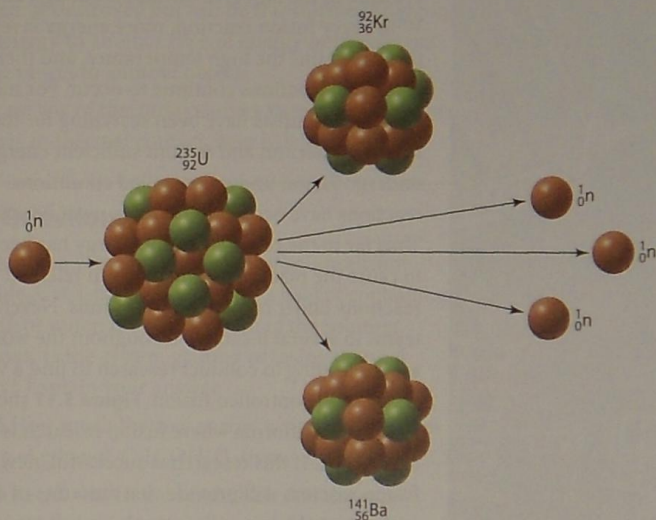


Figure 5.9 In this example, when a uranium-235 nucleus absorbs a neutron, it splits into a krypton-92 nucleus and a barium-141 nucleus and three neutrons. The krypton and barium isotopes are radioactive.

Nuclear Fusion

Another nuclear reaction occurs in the Sun. This process is called *nuclear fusion*. Two very small nuclei combine, or fuse, to form a slightly larger nucleus. The reaction that occurs most frequently in the Sun is the fusion of deuterium (${}^2_1\text{H}$) and tritium (${}^3_1\text{H}$), to form a very unstable helium-5 (${}^5_2\text{He}$), which immediately breaks down into helium-4 (${}^4_2\text{He}$) and a neutron (${}^1_0\text{n}$). The reaction is shown below and is also illustrated in **Figure 5.10**. The helium-4 that is produced is stable, and thus fusion does not produce radioactive materials.

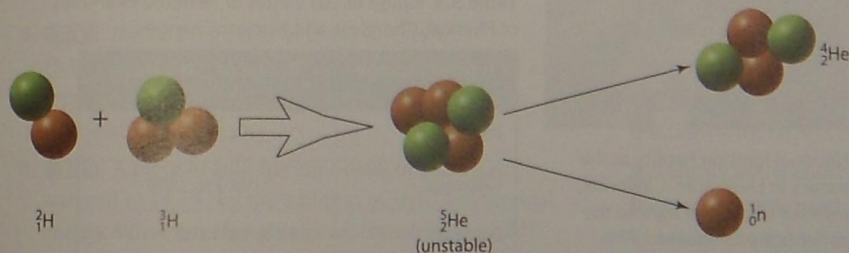
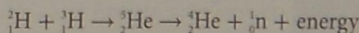


Figure 5.10 Many small nuclei undergo fusion to form a larger nucleus. This reaction is the most common reaction in the Sun.

The sum of the masses of helium-4 and the neutron is less than the sum of the masses of deuterium and tritium, and thus some mass has been converted into energy. When 1 mol of deuterium and 1 mol of tritium fuse, 1.7×10^9 kJ of energy is released. This value is approximately 10 times smaller than the energy released when 1 mol of uranium-235 fissions. However, the sum of the masses of deuterium and tritium is about 47 times smaller than the mass of uranium-235. Therefore, the energy released per unit mass is much larger for nuclear fusion than for nuclear fission. As well, nuclear fusion does not produce radioactive products.

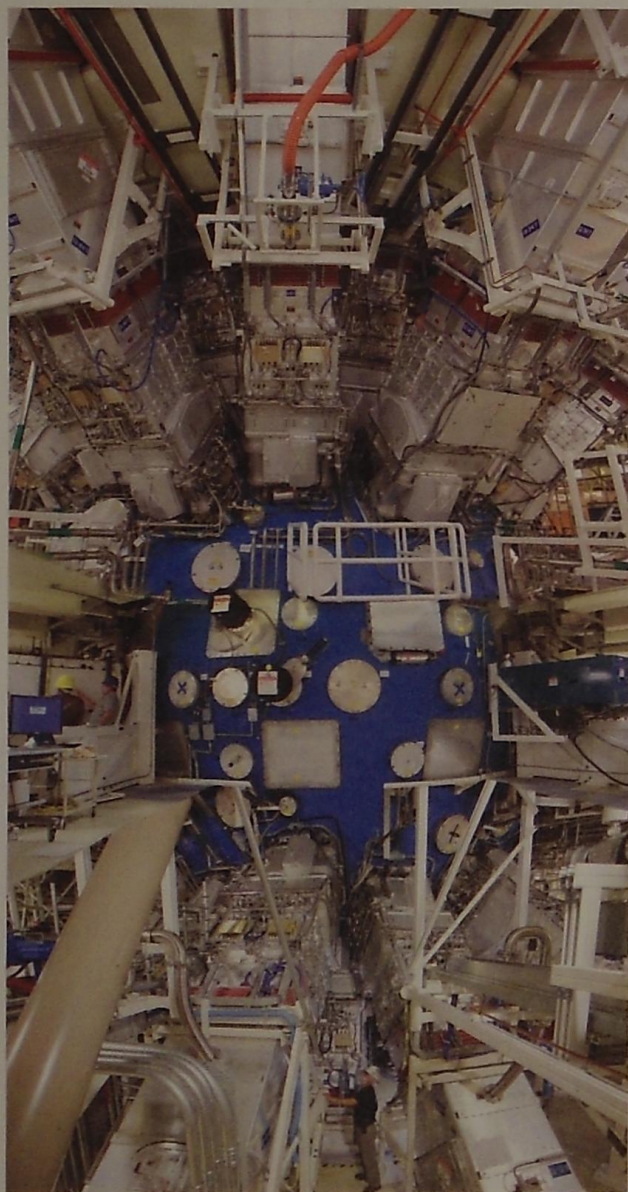


Figure 5.11 In March 2009, at the National Ignition Facility at the Lawrence Livermore National Laboratory in Livermore, California, a laser beam delivered 1.1 million joules of ultraviolet light to the target chamber where fusion experiments are conducted. This was the first time a fusion laser had delivered an amount of energy greater than one megajoule.

In order for two small atoms to undergo nuclear fusion, they must collide with a tremendous amount of kinetic energy. The extremely high temperature and pressure in the Sun give the atoms enough energy. With every fusion reaction, more energy is released that maintains the high temperature, and therefore the fusion reactions continue to occur. For more than 50 years, scientists have been searching for methods to give deuterium and tritium sufficient energy to undergo fusion under controlled conditions. These reactions have occurred but cannot yet be sustained. Thus far in the research, more energy has been used to cause the reactions than has been released by the reactions under controlled conditions. Nevertheless, teams in several locations throughout the world are continuing to conduct research to find a way to accomplish controlled fusion. **Figure 5.11** shows a facility in California where fusion research is being carried out. If this research is successful, new nuclear fusion reactors will provide vast amounts of energy without producing radioactive by-products or greenhouse gases.

Comparing Enthalpy Changes

Table 5.3 lists the ranges in the values of enthalpy changes for physical, chemical, and nuclear changes. Notice that enthalpy changes associated with physical changes are the smallest. Enthalpy changes associated with chemical changes are greater than those of physical changes but less than those of nuclear reactions. Enthalpy changes associated with nuclear changes are much greater than any other type of change.

Table 5.3 Range of ΔH Values of Selected Examples of Physical, Chemical, and Nuclear Changes

| Type of Change | Range of ΔH Values (kJ/mol) |
|----------------|--|
| Physical | ± 0.44 to ± 40.7 |
| Chemical | ± 196.4 to ± 890 |
| Nuclear | -1.13×10^8 to -2×10^{10} |

Note: The \pm signs indicate that the values can be positive or negative, depending on the direction of the change.

Section 5.1 Review

Section Summary

- A system is the object or substance being studied, and the surroundings are everything else in the universe. Systems can be open, closed, or isolated.
- Open and closed systems can exchange energy with the surroundings by doing work on the surroundings, or by the surroundings doing work on the system.
- The first law of thermodynamics states that energy cannot be created or destroyed but can be transformed from one type of energy to another type of energy or transferred from one object to another object.
- The second law of thermodynamics states that, when two objects are in thermal contact, heat will be transferred from the object at a higher temperature to the object at the lower temperature until they reach thermal equilibrium.
- An enthalpy change in a system, occurring at constant pressure, is the same as the amount of heat that is exchanged between the system and its surroundings. Enthalpy changes can be positive or negative and depend only on the initial and final states of the system.
- The range of enthalpy changes is lowest for physical changes, intermediate for chemical changes, and highest for nuclear changes.

Review Questions

1. **K/U** When a system consisting of solid calcium chloride, $\text{CaCl}_2(\text{s})$, is dissolved in a beaker containing 100 mL of water, the temperature of the solution increases. Is the system gaining or losing thermal energy? Explain your answer.
2. **T/I** How much thermal energy is required to warm 350.0 g of ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$, from -6.4°C to 21.7°C ?
3. **T/I** Recall that in the symbol ${}_Z^AX$, A is the mass number, Z is the atomic number, and X is the chemical symbol. Balance the nuclear equations below with the appropriate nuclear particle (${}_1^0\text{n}$, ${}_{-1}^0\text{e}$, ${}_1^1\text{p}$).
 - a. ${}_{6}^{14}\text{C} \rightarrow {}_{7}^{14}\text{N} + \text{_____}$
 - b. ${}_0^1\text{n} \rightarrow \text{_____} + {}_{-1}^0\text{e}$
 - c. ${}_{26}^{55}\text{Fe} + \text{_____} \rightarrow {}_{25}^{55}\text{Mn} + \text{energy}$
4. **A** Ethoxyethane, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(\ell)$, is a solvent that is slightly polar. Table salt, $\text{NaCl}(\text{s})$, is an ionic solid. Ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$, is moderately polar. Compare the mixing of table salt and ethanol with ethoxyethane. In which compound would you predict the solute-solvent attractions to be greater? How would this affect the enthalpy of solution, $\Delta H_{\text{solution}}$? Explain your answers in a few sentences.
5. **T/I** The melting point of $\text{O}_2(\text{s})$ is -219°C . Determine the amount of thermal energy that must be removed to completely freeze 15.0 mol $\text{O}_2(\ell)$ at this temperature.
6. **T/I** A piece of gold having a mass of 15.55 g is warmed to 14.7°C by the addition of 164.7 J of thermal energy. What was the initial temperature of the gold?
7. **T/I** By how much will the temperature of 2.00 kg of air change if it absorbs all of the heat given up when 1.00 kg of water cools from 40.0°C to 20.0°C ?
8. **K/U** State the first law of thermodynamics and express the law as an equation.
9. **T/I** A system does 500 J of work on its surroundings. At the same time, 500 J of energy enters the system. What is the change in energy of the system, ΔE_{system} ?
10. **A** For each of the processes listed, define a system and state the sign of the enthalpy change for the system. Explain your reasoning for each answer.
 - a. natural gas burning in a furnace
 - b. water boiling
 - c. moving from a seated position to a standing position
 - d. melted wax solidifying
 - e. hydrogen atoms undergoing nuclear fusion in the Sun
11. **C** Frost forms on the windshield of a car on a cold winter morning. This frost disappears with no evidence that liquid water forms. Draw an enthalpy diagram to illustrate the change.
12. **A** Refer to **Figure 5.8**. Explain the significance of the difference in the region between B and C compared with that between D and E. Use diagrams to support your explanation.
13. **K/U** Compare nuclear reactions with chemical reactions with respect to the following:
 - a. identity of the atoms in the reactants and products
 - b. type of atomic particles involved
 - c. energy change

Key Terms

calorimeter

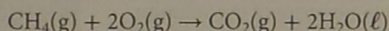
calorimetry

simple calorimeter

bomb calorimeter

In Section 5.1, you were introduced briefly to the enthalpy changes of chemical reactions. In this section and the next, you will focus on chemical reactions in more detail. First, consider the reason that enthalpy changes occur when a chemical reaction takes place. Although chemical reactions do not occur exactly as described below, it is valid to visualize a chemical reaction as happening in two steps.

In the first step of a chemical reaction, all chemical bonds are broken. In the second step, new bonds are formed. Energy is always needed to break bonds, so bond-breaking is endothermic. Energy is always released when bonds form, so bond-forming is exothermic. The amount of energy released or required varies greatly depending on the types of atoms and their bonding. For example, when a bond forms between a carbon atom and a hydrogen atom, the amount of energy released is quite different from the amount of energy released when a bond forms between an oxygen atom and a hydrogen atom. **Figure 5.12** shows the amount of energy needed to break all the bonds in a methane molecule and in two oxygen molecules. It also shows the energy released when bonds form between the same atoms in a different arrangement. A carbon dioxide molecule and two water molecules form. The difference between the total amount of energy used to break bonds and the total energy released when the bonds reform is equal to the enthalpy change of the reaction.



Under standard conditions, 890.8 kJ of heat is released when 1 mol of methane is combusted in 2 mol of oxygen, forming 1 mol of carbon dioxide and 2 mol of liquid water. As discussed on the next page, chemists have devised two different ways to include the enthalpy change in a chemical equation. In addition, you will see how an enthalpy diagram can help to visualize information related to enthalpy change.

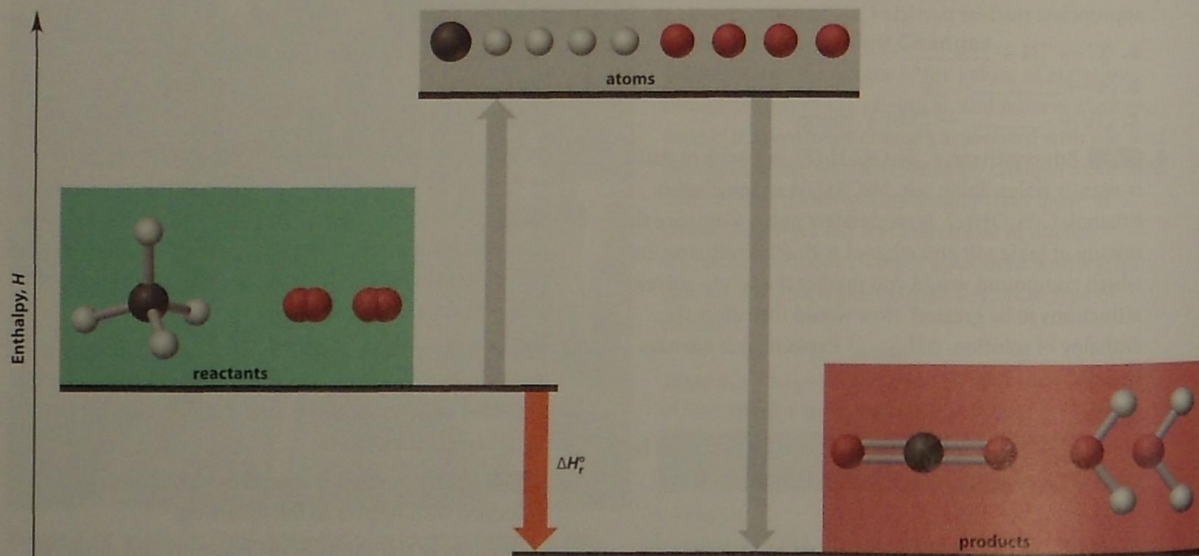
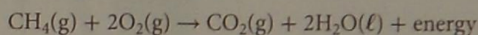


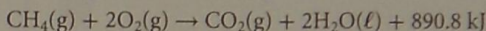
Figure 5.12 It takes less energy to break all of the bonds in a methane molecule and in two oxygen molecules compared with the energy that is released when the same atoms form a carbon dioxide molecule and two water molecules.

Thermochemical Equations

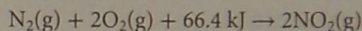
You have seen equations that include the word “energy,” such as the equation below, which indicates energy is released in this reaction.



To write a thermochemical equation, instead of writing “energy,” write the numerical value for the enthalpy change of the reaction, as shown.



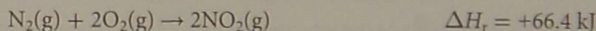
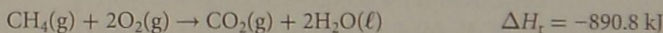
If energy is required to make a reaction proceed in the direction in which it is written, the enthalpy change term is on the left side of the equation. For example, the energy in lightning causes formation of nitrogen dioxide from oxygen and nitrogen in the air. The thermochemical equation is written as follows:



It is critical to correctly interpret the meaning of the energy indicated in a thermochemical equation. The total enthalpy change of a reaction depends on the amounts of reactants that are converted into products. Obviously, 1 mol of methane gas combusted in oxygen will not produce as much heat as will 50 mol of methane when combusted in oxygen. Thermochemical equations are written with the assumption that the coefficients of the reactants and products represent the amount in moles of each substance that is involved in the reaction. The second form of the equation above in which methane is combusted in oxygen reads, “1 mol of methane and 2 mol of oxygen react to produce 1 mol of carbon dioxide, 2 mol of water, and 890.8 kJ of heat.” A simpler way to read the equation uses the phrase “as written,” which implies that the coefficients represent the amount in moles of reactants and products. The equation above could be read, “The enthalpy change of the reaction between methane and oxygen, as written, is -890.8 kJ .”

ΔH Notation

You may also write the enthalpy term beside the chemical equation as shown here.



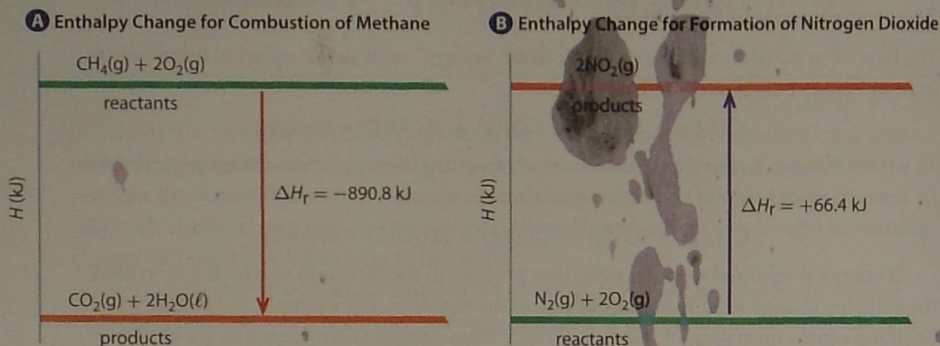
The subscript “r” means that this value represents the enthalpy change of a *reaction*. The ΔH notation also implies that the coefficients represent the amount in moles of the reactants and products that are involved in the reaction. Normally, you would not include the plus sign in the notation, but it is used in this example and throughout this textbook to emphasize the nature of the reaction being discussed.

Enthalpy Diagrams

Enthalpy diagrams can help you to visualize the relative enthalpies of the reactants and products and whether the reaction is endothermic or exothermic. The two diagrams in **Figure 5.13** (on the next page) represent the same reactions that you have seen above. Notice that the y -axis is the Enthalpy axis. It does not have a zero point, because it is not possible to know the absolute enthalpy of the compounds involved in the reaction. Only *changes in enthalpy* can be measured and therefore represented in a diagram. Also note that there is no x -axis in an enthalpy diagram, because the enthalpy change of a system depends only on the initial and final states of the system and is not affected by anything that occurs during the process.

When a reaction is exothermic (has a negative enthalpy change) the reactants have a larger enthalpy than the products and are therefore drawn above the products, as shown in **Figure 5.13A**. The arrow representing the enthalpy change points downward. When a reaction is endothermic (has a positive enthalpy change), the products have a larger enthalpy than the reactants. Therefore, the products are drawn above the reactants and the arrow representing the enthalpy change points upward, as shown in **Figure 5.13B**.

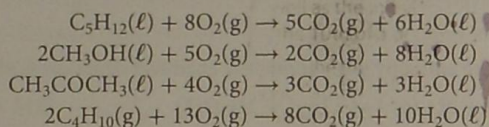
Figure 5.13 Chemists use the concept of enthalpy because it depends only on the initial and final states of a system that undergoes a process. Therefore, enthalpy diagrams need to represent only the initial and final conditions of the compounds in a chemical reaction. The processes that occur during the reaction do not affect the enthalpy change.



Molar Enthalpy of Combustion

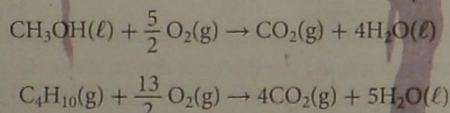
Combustion reactions are so important in thermochemistry that they are given their own symbol: ΔH_{comb} . You can find standard molar enthalpies of combustion ($\Delta H_{\text{comb}}^\circ$) in reference tables and many other sources of chemical data. Before you use these data, however, it is important to understand how to interpret the values. You know that the term “standard” means that the values are given for a temperature of 25°C and a pressure of 100 kPa. Since combustion reactions release a large amount of heat and the products are extremely hot, how can the values represent a reaction taking place under standard conditions? In determining the values, chemists have accounted for all of the steps that occur between the reactants at 25°C and 100 kPa of pressure, the combustion process, and products returning to 25°C and 100 kPa of pressure.

Another question arises when you consider the coefficients in reaction equations for combustion. For example, examine the following examples of combustion reactions:



If you interpret the coefficients as the amount in moles of substances involved in the reaction, you see that a widely varying amount in moles of reactants and products can be involved in a single reaction. Values for standard molar enthalpies of combustion listed in tables refer only to the compound that is undergoing combustion. For example, in the first equation above, the value that you would find in a table such as **Table 5.4** represents the enthalpy change that occurs when 1 mol of pentane, C_5H_{12} , is combusted. The amount in moles of the other reactant and the products are not considered in the enthalpy of combustion for a specific compound.

The values for enthalpy changes in a thermochemical equation or beside the equation with the ΔH notation are the values for the equation “as written.” In the second and fourth equations above, the methanol and the butane both have coefficients of 2. However, the $\Delta H_{\text{comb}}^\circ$ values in tables represent the combustion of 1 mol of the compound undergoing combustion. Thus, they do not fit the equations above “as written.” For that reason, you will sometimes see equations written with fractional coefficients, so the compound under consideration can be written with a coefficient of 1. For example, the second and fourth equations might be written as shown here, where all of the coefficients have been divided by 2.



No matter how an equation is written, the values in reference tables are always molar values. Some typical values of standard molar enthalpies of combustion are listed in **Table 5.4**.

Table 5.4 Some Representative Values of Standard Molar Enthalpy of Combustion*

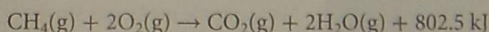
| Compound | Formula | $\Delta H^\circ_{\text{comb}}$ (kJ/mol) |
|---------------------|---|---|
| Methane | $\text{CH}_4(\text{g})$ | -890.8 |
| Ethane | $\text{C}_2\text{H}_6(\text{g})$ | -1560.7 |
| Propane | $\text{C}_3\text{H}_8(\text{g})$ | -2219.2 |
| Butane | $\text{C}_4\text{H}_{10}(\text{g})$ | -2877.6 |
| Pentane | $\text{C}_5\text{H}_{12}(\ell)$ | -3509.0 |
| Hexane | $\text{C}_6\text{H}_{14}(\ell)$ | -4163.2 |
| Heptane | $\text{C}_7\text{H}_{16}(\ell)$ | -4817.0 |
| Octane | $\text{C}_8\text{H}_{18}(\ell)$ | -5470.3 |
| Methanol | $\text{CH}_3\text{OH}(\ell)$ | -726.1 |
| Ethanol | $\text{C}_2\text{H}_5\text{OH}(\ell)$ | -1366.8 |
| Glycerol | $\text{CH}_2\text{OHCHOHCH}_2\text{OH}(\ell)$ | -1655.4 |
| Acetone | $\text{CH}_3\text{COCH}_3(\ell)$ | -1789.9 |
| Benzoic acid | $\text{C}_7\text{H}_6\text{O}_2(\text{s})$ | -3228.2 |
| Ammonia | $\text{NH}_3(\text{g})$ | -382.8 |
| Dinitrogen monoxide | $\text{N}_2\text{O}(\text{g})$ | -82.1 |

*Note: Because these are *standard* values, meaning that the reactants started at 25°C and the products ended at 25°C, the products are $\text{H}_2\text{O}(\ell)$ and $\text{CO}_2(\text{g})$. Many tables provide values that are not *standard* values.

Learning Check

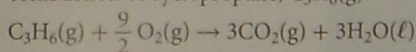
7. The standard molar enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, of a hydrocarbon is always a negative value. Is the enthalpy term included as a reactant or a product in thermochemical equations representing combustion reactions? How do you know?

8. For the reaction shown below, which has more potential energy: the reactants or the products? State a reason for your choice.



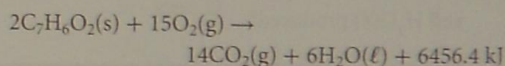
9. When ethane, $\text{C}_2\text{H}_6(\text{g})$, undergoes complete combustion to form carbon dioxide and water, the standard molar enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, is -1560.7 kJ/mol. Write the thermochemical equation for the combustion of ethane.

10. Sketch a potential energy diagram for the combustion of cyclopropane, $\text{C}_3\text{H}_6(\text{g})$.



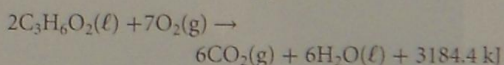
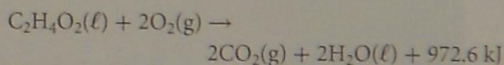
$$\Delta H^\circ_{\text{comb}} = -2091.3 \text{ kJ/mol}$$

11. The complete combustion of benzoic acid, $\text{C}_7\text{H}_6\text{O}_2(\text{s})$, is represented by the equation shown below.



What is the standard molar enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, per mole of benzoic acid?

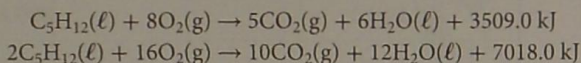
12. The equations representing complete combustion of the esters methyl methanoate, $\text{C}_2\text{H}_4\text{O}_2(\ell)$, and methyl ethanoate, $\text{C}_3\text{H}_6\text{O}_2(\ell)$, are as follows:



What is the standard molar enthalpy of combustion, $\Delta H^\circ_{\text{comb}}$, for the ester having the greater value for this property?

Reactant Amounts and Enthalpy of Reaction

A roaring bonfire releases more thermal energy than does a burning matchstick. The reaction is the same, but the quantities involved are different. *The enthalpy change associated with a reaction depends on the amounts of the reactants involved.* For example, the thermochemical equation for the combustion of pentane indicates that 3509.0 kJ of energy is released when 1 mol of pentane is combusted. The combustion of 2 mol of pentane releases twice as much energy, or 7018.0 kJ.



The enthalpy of a reaction is directly proportional to the amounts of the substances that react. That is, if the amounts of the reactants double, the enthalpy change also doubles. In other words, when you multiply the stoichiometric coefficients of a thermochemical equation by any factor, you must multiply the enthalpy term by the same factor.

If you know the thermochemical equation for a reaction, you can multiply the enthalpy term by the appropriate stoichiometric factor to predict the enthalpy change associated with the reaction for any amount of products or reactants. The enthalpy change for a reaction is equal to the amount in moles of a specified reactant or product times the enthalpy change for 1 mol of the specified reactant or product. Thus, the enthalpy change for a reaction can be expressed as follows:

The enthalpy change of a reaction is equal to the amount in moles, n , of a specified reactant or product multiplied by the standard molar enthalpy change for the specified reactant or product.

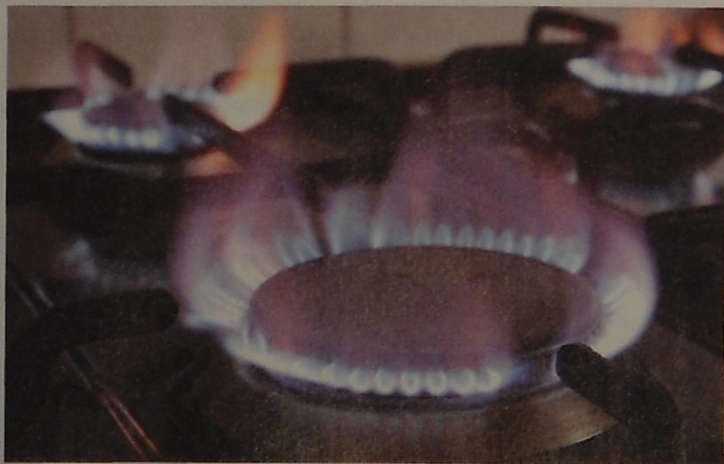
$$\Delta H_r = n\Delta H_r^\circ$$

If you know the enthalpy of a reaction, you can use it to determine the amounts of the reactants or products involved, as shown in the Sample Problems below.

Sample Problem

Calculating an Enthalpy Change

- What is the enthalpy change when a 50.00 g sample of methane undergoes complete combustion according to the equation $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$?
- What is the enthalpy of the reaction per mole of $\text{O}_2(\text{g})$ consumed, $\text{CO}_2(\text{g})$ produced, and $\text{H}_2\text{O}(\ell)$ produced?



Many people prefer gas stoves because it is easier to control the temperature of the food being cooked. Gas stoves burn natural gas, which is mostly methane.

What Is Required?

You need the enthalpy of combustion, ΔH_{comb} , for 50.00 g of methane.

You need the enthalpy of the reaction, ΔH_r , per mole of $\text{O}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\ell)$.

What Is Given?

You are given the mass of methane: $m = 50.00 \text{ g}$

You are given the balanced chemical equation: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$

You know that $\Delta H_{\text{comb}}^\circ = -890.8 \text{ kJ/mol}$ for methane (from Table 5.4)

| Plan Your Strategy | Act on Your Strategy |
|--|--|
| a. Determine the amount of methane by using its mass and its molar mass. | $n = \frac{m}{M}$ $= \frac{50.00 \text{ g}}{16.05 \frac{\text{g}}{\text{mol}}}$ $= 3.115 \text{ mol}$ |
| Multiply the standard molar enthalpy of combustion by the amount of methane to determine the enthalpy change associated with the combustion of 50.00 g of methane. | $\Delta H_{\text{comb}} = n\Delta H_{\text{comb}}^\circ$ $= (3.115 \text{ mol}) \left(\frac{-890.8 \text{ kJ}}{\text{mol}} \right)$ $= -2.775 \times 10^3 \text{ kJ}$ |

| Plan Your Strategy | Act on Your Strategy |
|--|--|
| b. Use the mole ratio of $\text{O}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$ to $\text{CH}_4(\text{g})$ to find the enthalpy of reaction per mole of the three compounds. | $\Delta H_r (\text{per mol O}_2) = \left(\frac{n_{\text{CH}_4}}{n_{\text{O}_2}} \right) \left(\frac{\Delta H_{\text{comb}}^\circ}{n_{\text{CH}_4}} \right)$ $= \left(\frac{1 \text{ mol CH}_4}{2 \text{ mol O}_2} \right) \left(\frac{-890.8 \text{ kJ}}{1 \text{ mol CH}_4} \right)$ $= -445.4 \text{ kJ}$ $\Delta H_r (\text{per mol CO}_2) = \left(\frac{n_{\text{CH}_4}}{n_{\text{CO}_2}} \right) \left(\frac{\Delta H_{\text{comb}}^\circ}{n_{\text{CH}_4}} \right)$ $= \left(\frac{1 \text{ mol CH}_4}{1 \text{ mol CO}_2} \right) \left(\frac{-890.8 \text{ kJ}}{1 \text{ mol CH}_4} \right)$ $= -890.8 \text{ kJ}$ $\Delta H_r (\text{per mol H}_2\text{O}) = \left(\frac{n_{\text{CH}_4}}{n_{\text{H}_2\text{O}}} \right) \left(\frac{\Delta H_{\text{comb}}^\circ}{n_{\text{CH}_4}} \right)$ $= \left(\frac{1 \text{ mol CH}_4}{2 \text{ mol H}_2\text{O}} \right) \left(\frac{-890.8 \text{ kJ}}{1 \text{ mol CH}_4} \right)$ $= -445.4 \text{ kJ}$ |

Check Your Solution

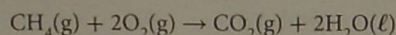
The units are correct. The sign of the enthalpy change is negative, which makes sense because a hydrocarbon combustion reaction is always exothermic. The enthalpy change for the reaction is about three times as great as the molar enthalpy of combustion, which makes sense because about 3 mol of methane was combusted.

Sample Problem

Using Enthalpy Data to Determine the Mass of Products

Problem

When methane is combusted, along with the heat produced, oxygen is consumed. Determine the mass of oxygen consumed if the total change in enthalpy of the reaction is $-2.50 \times 10^2 \text{ kJ}$, given the equation:



What Is Required?

You need to determine the mass of oxygen consumed in a reaction in which the total enthalpy change is $-2.50 \times 10^2 \text{ kJ}$.

What Is Given?

You know the chemical equation for the reaction: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$

You know that $\Delta H^\circ_{\text{comb}} = -890.8 \text{ kJ/mol}$ for methane (from Table 5.4).

You also know the total enthalpy change for the given reaction: $\Delta H_r = -2.50 \times 10^2 \text{ kJ}$

| Plan Your Strategy | Act on Your Strategy |
|---|--|
| Determine the amount in moles of methane combusted by using the formula $\Delta H_r = n\Delta H^\circ_{\text{comb}}$. | $\Delta H_r = n\Delta H^\circ_{\text{comb}}$ $n = \frac{\Delta H_r}{\Delta H^\circ_{\text{comb}}}$ $= \frac{-2.50 \times 10^2 \text{ kJ}}{-890.8 \frac{\text{kJ}}{\text{mol}}}$ $= 0.2806 \text{ mol}$ |
| Find the amount in moles of oxygen consumed from the ratio of coefficients and the calculated amount in moles of methane combusted. | $\frac{n_{\text{O}_2}}{n_{\text{CH}_4}} = \frac{n_{\text{O}_2 \text{ consumed}}}{n_{\text{CH}_4 \text{ combusted}}}$ $\frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = \frac{n_{\text{O}_2 \text{ consumed}}}{0.2806 \text{ mol CH}_4}$ $n_{\text{O}_2 \text{ consumed}} = \left(\frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} \right) (0.2806 \text{ mol CH}_4)$ $= 0.5612 \text{ mol O}_2$ |
| Find the mass of oxygen by using its molar mass and of its amount in moles. | $n = \frac{m}{M}$ $m = nM$ $= (0.5612 \text{ mol}) \left(32.00 \frac{\text{g}}{\text{mol}} \right)$ $= 17.9584 \text{ g}$ $= 18.0 \text{ g}$ <p>Therefore, 18.0 g of oxygen is consumed when the total enthalpy change of the combustion of methane is $-2.50 \times 10^2 \text{ kJ}$.</p> |

Check Your Solution

The units are correct. The mass of oxygen produced is less than the mass of 2 mol $\text{O}_2(\text{g})$, which is 64 g. This makes sense, because the enthalpy change of the reaction was less than $\Delta H^\circ_{\text{comb}}$.

Practice Problems

- Pentane reacts with an excess of oxygen to produce carbon dioxide and water vapour. What is the enthalpy change of the reaction per mole of each of the following gases? The enthalpy of combustion for pentane, $C_5H_{12}(l)$, is -3509.0 kJ/mol .
 - oxygen
 - carbon dioxide
 - water
- What is the enthalpy change when 4.608 g of ethanol, $C_2H_5OH(l)$, undergoes complete combustion?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) + 13\,668 \text{ kJ}$$
- Determine the thermal energy released by the combustion of each of the following samples of hydrocarbons to $CO_2(g)$ and $H_2O(l)$.
 - 56.78 g of hexane, $C_6H_{14}(l)$
 - 1.36 kg of octane, $C_8H_{18}(l)$
 - $2.344 \times 10^4 \text{ g}$ of heptane, $C_7H_{16}(l)$
- What is the enthalpy change for the combustion of a 1.00 g sample of methane, $CH_4(g)$, under standard conditions?
- Naphthalene, $C_{10}H_8(s)$, is an organic compound used in the manufacture of dyes, plastics, and some insecticides. What mass of this compound will release 500.0 kJ of thermal energy?

$$C_{10}H_8(s) + 12O_2 \rightarrow 10CO_2(g) + 4H_2O(l) + 5156 \text{ kJ}$$
- What mass, in kilograms, of methanol must be combusted to generate $5.39 \times 10^5 \text{ kJ}$ of thermal energy?
- Answer the questions for the combustion of propene, $C_3H_6(g)$, using the following equation:

$$2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) + 4116.0 \text{ kJ}$$
 - Determine the standard molar enthalpy of combustion of propene.
 - What is the maximum amount of thermal energy available from the combustion of 5.00 g of $C_3H_6(g)$?
- When 0.050 mol of a hydrocarbon undergoes complete combustion, 110.95 kJ of heat is given off.
 - What is the enthalpy of combustion for this hydrocarbon?
 - Refer to **Table 5.4** and identify the hydrocarbon.
- What mass of butane, $C_4H_{10}(g)$, must undergo complete combustion to produce 1.00 MJ of heat according to the following equation?

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) + 2877.6 \text{ kJ}$$
- The standard molar enthalpy of combustion of propan-2-ol, $CH_3CH(OH)CH_3(l)$, is -2006 kJ/mol .
 - Write the thermochemical equation for the combustion of 1 mol of this compound to form carbon dioxide and water.
 - How much heat is given off when 25.00 g of water is produced?

Using Calorimetry To Study Energy Changes

A **calorimeter** is a device that is used to measure the heat released or absorbed by a physical or chemical process taking place within it. **Calorimetry** involves the use of a calorimeter to study the energy changes associated with physical processes and chemical reactions. The term *calorimeter* comes from the word *calorie*, which was the original unit for heat transferred from one object to another.

A calorie is defined as the amount of heat needed to increase the temperature of one gram of water by one degree Celsius. A calorie is not an SI unit, so most scientists no longer use it. However, many dieticians and nutritionists still use the calorie to communicate the amount of energy available in foods. When you see “Calories” written on food labels, it has a capital C, which means 1000 calories. One calorie is equal to 4.184 J and 1 Calorie is equal to 4.184 kJ .

calorimeter a device used to measure the heat released or absorbed during a chemical or physical process occurring within it

calorimetry the technological process of measuring the heat released or absorbed during a chemical or physical process

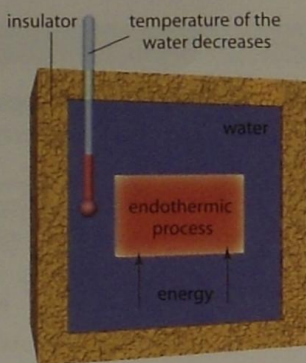


Figure 5.14 If an endothermic process occurs, heat will be transferred from the water to the system in which the process occurs. Because heat was lost, the temperature of the water is reduced.

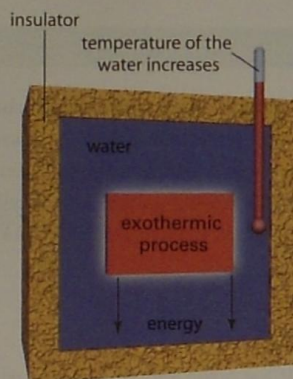


Figure 5.15 If an exothermic process occurs in the calorimeter, heat will be transferred from the process to the water. Because heat was gained by the water, the temperature increases.

Ideally, a calorimeter is an isolated system, which does not allow products to escape or thermal energy to be transferred to the air or other materials surrounding it. **Figures 5.14** and **5.15** model how a calorimeter works. You can consider the water to be one system and the container in which the process is occurring as another system. The two systems are in thermal contact, but they are isolated from the surroundings.

The Theoretical Basis of Calorimetry

Calorimetry is based on the two laws of thermodynamics. Recall that the first law of thermodynamics, also known as the law of conservation of energy, states that the energy of the universe is constant. This law ensures that any energy added to a system came from the surroundings and, likewise, any energy lost by a system went to the surroundings. In relationship to calorimetry, the most useful statement of the second law of thermodynamics is stated in the following box.

Second Law of Thermodynamics

Thermal energy is spontaneously transferred from an object at a higher temperature to an object at a lower temperature until the two objects reach the same temperature.

This law ensures that the temperature that you measure after a process has taken place is the equilibrium temperature of all systems that are in thermal contact. It follows then that as energy is released (or absorbed) by a chemical reaction in a calorimeter, it will result in a change in the temperature of the calorimeter surrounding the reaction. Therefore, the enthalpy of a reaction can be calculated based on the thermal energy transfer in the calorimeter.

Using a Simple Calorimeter

A **simple calorimeter** consists of two stacked vessels such as polystyrene cups covered with a lid, as shown in **Figure 5.16**. This type of calorimeter can yield reasonably accurate results if used carefully. The reaction occurs in the inner cup, which contains a known mass of water. The polystyrene cups prevent the escape of thermal energy because they are excellent insulators. The air trapped between the inner cup and the outer cup provides additional insulation. Liquid products remain inside the inner cup. However, gases can escape because the lid has holes for the thermometer and stirrer. Because the calorimeter allows gases to escape (or enter) it, this calorimeter measures the thermal energy changes of processes at a constant pressure.

simple calorimeter a calorimeter made of two stacked vessels covered by a lid with holes in the top just large enough for a thermometer and a stirrer

Assumptions That Are Made

When using a simple calorimeter, the process that you are studying often involves compounds that are dissolved directly in the water. You are measuring the temperature change of the water in which a process such as a chemical reaction is occurring. To calculate the amount of heat transferred from the chemical reaction to the water, you must use the specific heat capacity of the water. Therefore, the solution must be dilute so that the presence of the reactants and the products does not significantly change the specific heat capacity of the water. When using a simple calorimeter, you must make the following assumptions:

- The system is isolated. (Any thermal energy that is exchanged with the surroundings outside the calorimeter is small enough to be ignored.)
- The thermal energy that is exchanged with the calorimeter polystyrene cups, thermometer, lid, and stirring rod is small enough to be ignored.
- If something dissolves or reacts with the water in the calorimeter, the resulting solution retains the properties of water. (For example, density and specific heat capacity remain the same.)
- The process takes place under constant pressure.

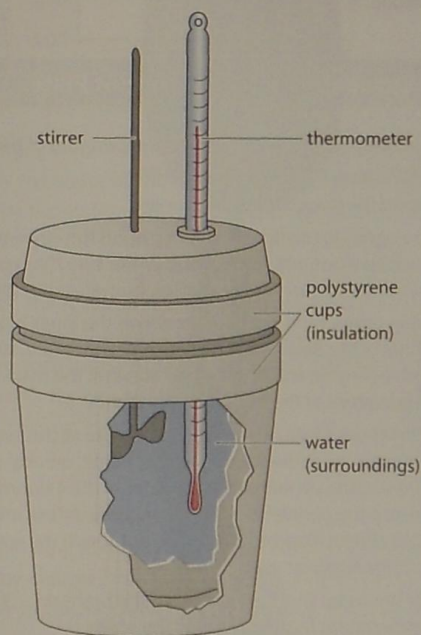


Figure 5.16 A simple calorimeter can be made from stacked polystyrene cups. It is helpful to place the calorimeter in a beaker to reduce the chance that it will tip over. *Infer* why it is important to keep the holes in the lid for the stirrer and thermometer as small as possible.

Once you make these assumptions, the following equations apply:

$$\begin{aligned}\text{thermal energy released by the system} &= -\text{thermal energy absorbed by the surroundings} \\ \text{heat lost (or gained) by the system} &= -\text{heat gained (or lost) by the surroundings}\end{aligned}$$

The system is the chemical reaction (or physical change) that you are studying. The surroundings consist of the water in the calorimeter. When a chemical reaction releases or absorbs thermal energy in a calorimeter, the change in temperature is measured by a thermometer in the water. If you know the mass of the water and its specific heat capacity, you can calculate the change in thermal energy caused by the chemical reaction by using the equation $Q = mc\Delta T$.

How To Use a Simple Calorimeter

A simple calorimeter can measure thermal energy changes during chemical reactions, such as neutralization or displacement reactions, or during physical processes that involve a change in temperature. The following four steps outline how to use a simple calorimeter.

1. Ensure that the water in the calorimeter and all other solutions are equilibrated to room temperature before starting any investigation. Measure the initial temperature of the water in the calorimeter.
2. Add the reactants to the calorimeter. The water surrounds, and is in direct contact with, the chemical reaction (or physical change) that releases or absorbs thermal energy.
3. Allow the reaction to proceed. Stir the solution to ensure an even temperature throughout. The system is at a constant pressure because it is open to the air. Record the changing temperature of the water as the reaction proceeds. Identify the maximum or minimum temperature recorded. This temperature is the final temperature.
4. For an exothermic reaction, the final temperature is the maximum temperature recorded. It is used to calculate the thermal energy released. For an endothermic reaction, the final temperature is the minimum temperature recorded. It is used to calculate the thermal energy absorbed.

Activity 5.2

Determining the Temperature of a Bunsen Burner Flame or Hot Plate

In this activity, you will heat a sample of copper, contained within two pennies, in a Bunsen burner flame or on a hot plate. Once the copper is at the same temperature as the source of heat, you will transfer the copper to a known amount of water, at a known temperature. The heat lost by the copper is equal to the heat gained by the water.

Safety Precautions



- Wear safety eyewear and a lab coat or apron.
- Tie back hair or any loose clothing.
- Use EXTREME CAUTION when you are near an open flame.

Materials

- two pre-1997 Canadian copper pennies
- 100 mL water
- simple calorimeter (see **Figure 5.16**; two nested polystyrene cups in a 250 mL beaker, with a two-holed polystyrene lid)
- 100 mL graduated cylinder
- thermometer (alcohol or digital)
- electronic centigram balance
- Bunsen burner with igniter, or electric hot plate
- metal tongs (or tweezers if using a hot plate)
- stirring rod

Procedure

1. Read the procedure and prepare a suitable data table.
2. Using the 100 mL graduated cylinder, carefully measure out 100 mL of water and pour this volume into your calorimeter. Record the volume of water in the

calorimeter. Measure the initial temperature of the water, T_{initial} , to the nearest degree.

3. Record the mass of the two pennies.
4. After igniting the Bunsen burner, open the air vents to achieve optimal combustion. Make sure that your calorimeter is next to the Bunsen burner, or hot plate.
5. Using tongs, hold the pennies above the inner blue “cone” of the flame. (If you are using a hot plate, lay each penny on top of the hot plate until the maximum temperature of the hot plate is reached.)
6. After about 1 min, when the pennies are at the same temperature as the Bunsen burner flame, quickly immerse the pennies into the water in the calorimeter. Release the pennies slowly so that they do not melt the sides of the calorimeter. Do not touch the water with the tongs or tweezers.
7. Stir the water thoroughly and record the highest temperature, T_{final} , reached by the water.

Questions

1. At the end of the experiment, what is the temperature of the copper relative to the temperature of the water?
2. Define T_{final} , T_{initial} , and ΔT .
3. How does the temperature of the copper compare with that of the Bunsen burner flame (or hot plate surface) after the copper and the flame have been in contact for 1 min?
4. Use your data to calculate the temperature of the Bunsen burner flame or of the surface of the hot plate. The specific heat capacity of water is $4.19 \text{ J/g} \cdot ^\circ\text{C}$; the specific heat capacity of copper is $0.385 \text{ J/g} \cdot ^\circ\text{C}$; the density of water is 1.00 g/mL . (Hint: Set up the equation: $\Delta H_{\text{Cu}} = -\Delta H_{\text{H}_2\text{O}}$.)
5. What assumptions did you make in your calculations?

Using Calorimetry Data To Determine the Enthalpy of Reaction

A simple calorimeter is well suited to determine the enthalpy changes of reactions in dilute aqueous solutions. The water in the calorimeter absorbs or provides the energy that is released or absorbed by a chemical reaction. When carrying out an experiment in a dilute solution, *the solution itself* absorbs or releases the energy. You can calculate the quantity of thermal energy that is absorbed or released by the solution using the equation $Q = mc\Delta T$. The mass, m , is the mass of the water or solution. *If the solution is dilute, you can assume the solution has the same specific heat capacity as water.* This assumption cannot be made for a concentrated solution because the specific heat capacity decreases when the concentration of a solute increases. For example, **Figure 5.17** shows a graph of the concentration of sodium chloride versus the specific heat capacity of the solution.

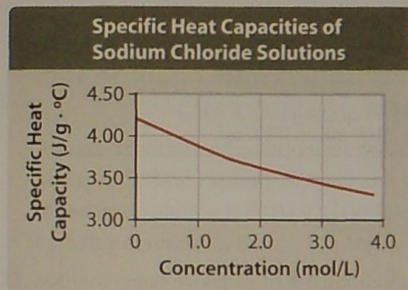


Figure 5.17 As the concentration of sodium chloride increases, the specific heat capacity of the solution decreases.

$Q = m_w c_w \Delta T_w$ is used to determine the quantity of thermal energy absorbed or released by the water in the calorimeter. To find the quantity of thermal energy released or absorbed by the system, just change the sign of the calculated value for Q .

You can use the data collected from a calorimetry experiment to determine the molar enthalpy of reaction, ΔH_r , for a reaction that has taken place in the calorimeter. In a simple calorimeter, the reaction takes place at constant pressure; therefore, the heat, Q , exchanged by the system and the water is equal to the experimental enthalpy change of the system (the compounds involved in the reaction), ΔH . To find the molar enthalpy change of the reaction, solve for ΔH_r in the equation:

$$\Delta H = n\Delta H_r$$
$$\Delta H_r = \frac{\Delta H}{n}$$

Recall that n is the amount in moles of the specified reactant or product.

The following Sample Problem shows how calorimetry data can be used to calculate the enthalpy change of a chemical reaction in solution. Notice that all the materials in the calorimeter in the Sample Problem have the same final temperature.

Suggested Investigation

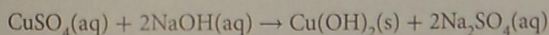
Plan Your Own
Investigation 5-A,
Determining the Enthalpy
of a Neutralization Reaction

Sample Problem

Determining the Enthalpy Change of a Reaction

Problem

Aqueous copper(II) sulfate, $\text{CuSO}_4(\text{aq})$, reacts with sodium hydroxide, $\text{NaOH}(\text{aq})$, in a double displacement reaction. A precipitate of copper(II) hydroxide, $\text{Cu}(\text{OH})_2(\text{s})$, and aqueous sodium sulfate, $\text{Na}_2\text{SO}_4(\text{aq})$, is produced:



A 50.00 mL volume of 0.300 mol/L $\text{CuSO}_4(\text{aq})$ is mixed with 50.00 mL of $\text{NaOH}(\text{aq})$ solution that contains an excess of $\text{NaOH}(\text{aq})$. The initial temperature of both solutions is 21.40°C. After mixing the solutions in a simple calorimeter, the highest temperature reached is 24.60°C. Determine the enthalpy change for the reaction as written and write the reaction's thermochemical equation.

Continued on next page >

What Is Required?

You need to calculate ΔH_r for the reaction as written.

You need to write the thermochemical equation for the reaction.

What Is Given?

You know the volume of $\text{CuSO}_4(\text{aq}) = 50.00 \text{ mL}$

You know the concentration of $\text{CuSO}_4(\text{aq}) = 0.300 \text{ mol/L}$

You know the volume of $\text{NaOH}(\text{aq}) = 50.00 \text{ mL}$

You know that there is an excess of $\text{NaOH}(\text{aq})$

You know the initial temperature, $T_{\text{initial}} = 21.40^\circ\text{C}$

You know the final temperature, $T_{\text{final}} = 24.60^\circ\text{C}$

You have the specific heat capacity of $\text{H}_2\text{O}(\ell)$: $4.19 \text{ J/g}\cdot^\circ\text{C}$ (see **Table 5.1**)

| Plan Your Strategy | Act on Your Strategy |
|---|---|
| Determine the total volume of the $\text{CuSO}_4(\text{aq})$ solution and the $\text{NaOH}(\text{aq})$ solution in the calorimeter. | $V_{\text{total}} = V_{\text{CuSO}_4} + V_{\text{NaOH}}$ $= 50.00 \text{ mL} + 50.00 \text{ mL} = 100.0 \text{ mL}$ |
| Determine the mass of the solution in the calorimeter, assuming the density is the same as the density of water (1.00 g/mL). | $m = Vd$ $= (100.0 \text{ mL}) \left(1.00 \frac{\text{g}}{\text{mL}} \right)$ $= 100.0 \text{ g}$ |
| Determine the amount in moles of $\text{CuSO}_4(\text{aq})$ present. | $n = cV$ $= \left(0.300 \frac{\text{mol}}{\text{L}} \right) (50.00 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right)$ $= 0.0150 \text{ mol}$ |
| Determine the change in thermal energy of the surroundings (water). | $Q = m_{\text{solution}} c_{\text{solution}} \Delta T_{\text{solution}}$ $= (100.0 \text{ g}) \left(4.19 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \right) (24.60^\circ\text{C} - 21.40^\circ\text{C})$ $= 1.341 \times 10^3 \text{ J}$ $= 1.341 \text{ kJ}$ |
| Determine the ΔH of the system (the compounds in the reaction). Change the sign of Q to find the change in thermal energy of the system. This value is equivalent to the ΔH of the system. | $\Delta H_{\text{system}} = -Q_{\text{solution}}$ $= -1.341 \text{ kJ}$ |
| Find ΔH_r by using the formula $\Delta H = n\Delta H_r$. Use the amount in moles of $\text{CuSO}_4(\text{aq})$. | $\Delta H = n\Delta H_r$ $\Delta H_r = \frac{\Delta H}{n}$ $= \frac{-1.341 \text{ kJ}}{0.0150 \text{ mol}}$ $= -89.4 \text{ kJ/mol}$ |
| Write the thermochemical equation for the reaction. Because the coefficient of $\text{CuSO}_4(\text{aq})$ is 1, ΔH_r represents the enthalpy change when 1 mol of copper(II) sulfate reacts with an excess of sodium hydroxide. | $\text{CuSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow$ $\text{Cu}(\text{OH})_2(\text{s}) + 2\text{Na}_2\text{SO}_4(\text{aq}) + 89.4 \text{ kJ}$ |

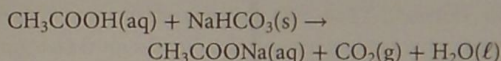
Check Your Solution

The solution has the correct number of significant digits. The units are correct. You know that the reaction was exothermic, because the temperature of the solution increased. The calculated value of ΔH is negative, which is correct for an exothermic reaction.

Practice Problems

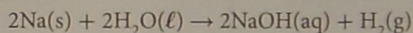
21. A pellet of potassium hydroxide, KOH(s) , having a mass of 0.648 g, is dissolved in 40.0 mL of water in an insulated cup. The temperature of the water increases from 22.6°C to 27.8°C. What is the molar enthalpy of solution, $\Delta H_{\text{solution}}$, for KOH(s) ? Assume that the solution has a density and a specific heat capacity equal to that of water.

22. When 5.022 g of sodium hydrogen carbonate, $\text{NaHCO}_3\text{(s)}$, reacts completely with 80.00 mL of acetic acid, $\text{CH}_3\text{COOH(aq)}$, the temperature increases from 18.6°C to 28.4°C.



Assume that the acid solution has the same density and specific heat capacity as water and that the mass of the final solution is 80.00 g. Calculate the molar enthalpy of reaction, ΔH_r .

23. Sodium reacts violently to form sodium hydroxide when placed in water, as shown in the following equation:



Determine an experimental value for the molar enthalpy of reaction for sodium given the following data:

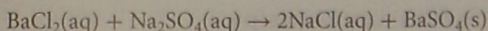
mass of sodium, Na(s) : 0.37 g

mass of water in calorimeter: 175 g

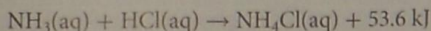
initial temperature of water: 19.30°C

final temperature of mixture: 25.70°C

24. In a simple calorimeter, 250.0 mL of 0.120 mol/L barium chloride, $\text{BaCl}_2\text{(aq)}$, is mixed with 150.0 mL of 0.200 mol/L sodium sulfate, $\text{Na}_2\text{SO}_4\text{(aq)}$. A precipitate of barium sulfate, $\text{BaSO}_4\text{(s)}$, forms. The initial temperature of the two solutions is 20.00°C. After mixing, the final temperature of the solutions is 20.49°C. Calculate the enthalpy of reaction, in kilojoules per mole, of $\text{Na}_2\text{SO}_4\text{(aq)}$. Assume that the solutions have densities and specific heat capacities equivalent to those of water.

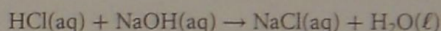


25. A neutralization reaction occurs when 100.0 mL of 0.200 mol/L aqueous ammonia, $\text{NH}_3\text{(aq)}$, and 200.0 mL of 0.200 mol/L hydrochloric acid, HCl(aq) , are mixed in an insulated cup.



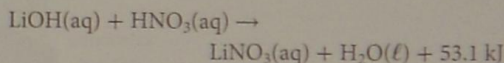
Assuming that the two solutions have the same density and specific heat capacity as water, what temperature change is expected after mixing?

26. In a simple calorimeter, 150.0 mL of 1.000 mol/L NaOH(aq) is mixed with 150.0 mL of 1.000 mol/L HCl(aq) . If both solutions were initially at 25.00°C and after mixing the temperature increased to 30.00°C, what is the enthalpy of reaction as written? Assume that the solutions have a density of 1.000 g/mL and a specific heat capacity of 4.19 J/g·°C.



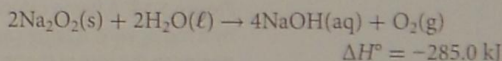
27. The enthalpy of solution for sodium hydroxide, NaOH(s) , is given as -55.0 kJ/mol. A chemist prepares 250.0 mL of a 0.100 mol/L solution of NaOH(aq) . Assuming that this solution has the same specific heat capacity and density as water, by how much should the water temperature increase as the NaOH(s) dissolves?

28. A neutralization reaction occurs when 120.00 mL of 0.500 mol/L LiOH and 160.00 mL of 0.375 mol/L $\text{HNO}_3\text{(aq)}$ are mixed in an insulated cup. Initially, the solutions are at the same temperature. If the highest temperature reached during mixing was 24.5°C, what was the initial temperature of the solutions?

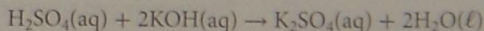


Assume that both of these solutions have a density of 1.00 g/mL and a specific heat capacity of 4.19 J/g·°C.

29. Peroxides will react to release oxygen when added to water. By how much would the water temperature change if 7.800 g of sodium peroxide, $\text{Na}_2\text{O}_2\text{(s)}$, is added to 110.00 mL of water?



30. In an insulated calorimeter, 200.0 mL of 1.00 mol/L potassium hydroxide, KOH(aq) , is mixed with an equal volume of 1.00 mol/L sulfuric acid, $\text{H}_2\text{SO}_4\text{(aq)}$. The temperature increases by 6.50°C. Assume that the solutions have the same density and specific heat capacity as water.



What is the molar enthalpy of neutralization?

Using Flame Calorimetry To Determine the Enthalpy of Combustion

You can use a flame calorimeter, such as the one shown in **Figure 5.18**, to determine the enthalpy of combustion of a substance that is burning. Unlike a simple calorimeter, a flame calorimeter is fire-resistant. It does, however, absorb a significant amount of energy; therefore, the heat absorbed by the calorimeter itself must be included in energy calculations. The fuel being tested is burned under a small can, heating both the can and the water inside.

For pure substances, the molar enthalpy of combustion is used. For substances that are not pure, such as most foods, the enthalpy of combustion is expressed in kJ/g rather than kJ/mol. Another appropriate way to express the enthalpy of combustion for food is in kJ/serving.

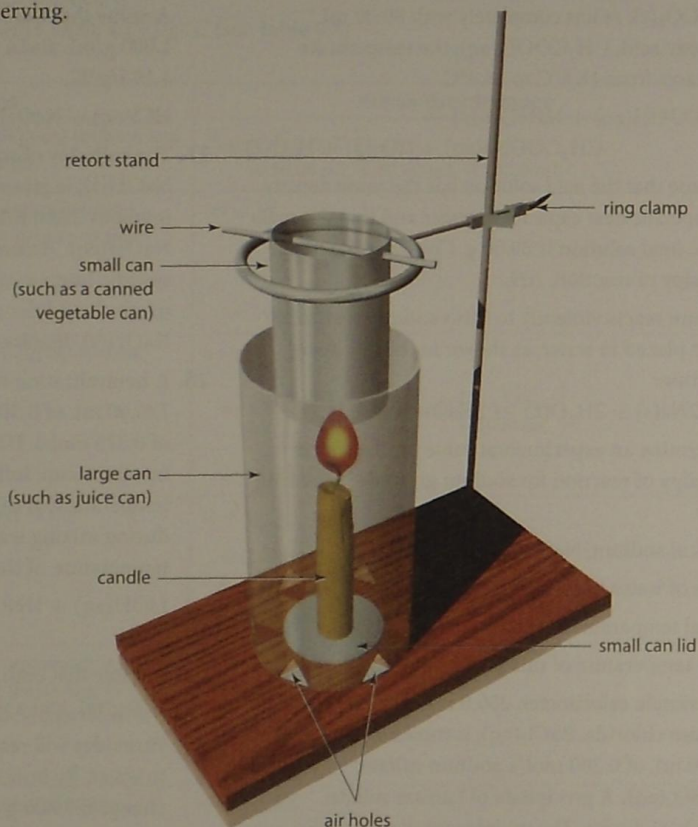


Figure 5.18 A flame calorimeter is commonly made from a small can suspended on a ring stand by a rod or wire. A large can with air holes surrounds the fuel source to direct the heat upward to minimize the loss of thermal energy to the surroundings. Nevertheless, there will be some loss of heat to the surroundings.

Analyze why the tip of the flame should just touch the bottom of the small can.

Using Bomb Calorimetry To Measure Enthalpy Changes during Combustion

To precisely and accurately measure the enthalpy changes of combustion reactions, chemists use a calorimeter called a **bomb calorimeter**, shown in **Figure 5.19**. A bomb calorimeter measures enthalpy changes during combustion reactions at a constant volume.

The bomb calorimeter works on the same general principle as the simple calorimeter. The reaction, however, takes place inside an inner metal chamber, called a **bomb**. This bomb contains pure oxygen. The reactants are ignited using an electric coil. A known quantity of water surrounds the bomb and absorbs the energy released by the reaction.

bomb calorimeter a device that measures heat released during a combustion reaction at a constant volume

A bomb calorimeter has many more parts than a simple calorimeter has. All these parts can absorb or release small quantities of energy. Therefore, you cannot assume that the heat lost to these parts is small enough to be negligible. To obtain precise heat measurements, you must know or find out the heat capacity, C , of the entire bomb calorimeter. A bomb calorimeter is calibrated for a constant mass of water. Because the mass of the other parts remains constant, there is no need for mass units in the heat capacity value. The units of C are joules per degree Celsius, or $\text{J}/^\circ\text{C}$, because the mass of all parts of the calorimeter are included in C . The heat capacity of a bomb calorimeter takes into account the heat that *all* parts of the calorimeter can lose or gain, as shown by the equation below:

$$C_{\text{bomb calorimeter}} = C_{\text{water}} + C_{\text{thermometer}} + C_{\text{stirrer}} + C_{\text{container}}$$

The value of the heat capacity for a particular calorimeter is generally provided by the manufacturer. Because the heat capacity (C) accounts for the mass of the calorimeter, C is equivalent to mc in the equation $Q = mc\Delta T$. Therefore, when performing calculations involving data from a bomb calorimeter, you can write the equation as $Q = C\Delta T$.

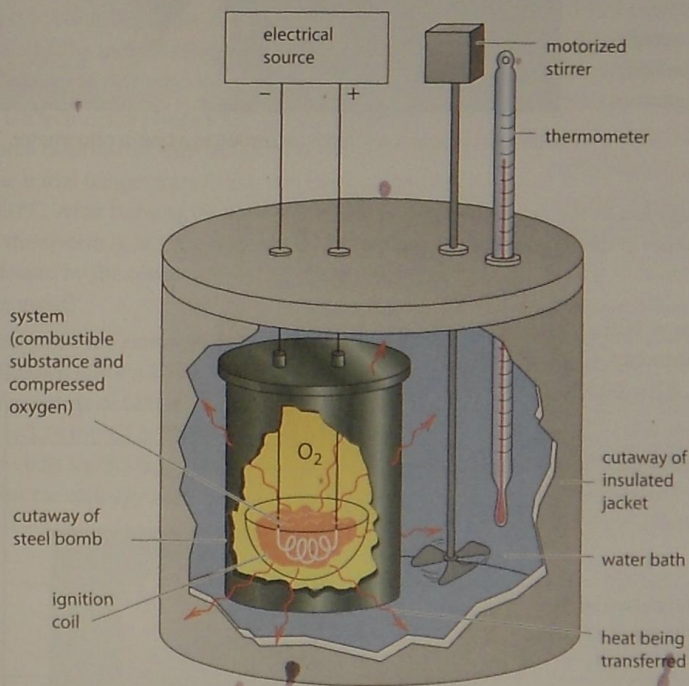


Figure 5.19 A bomb calorimeter is more sophisticated than a simple calorimeter or a flame calorimeter because it is an isolated system—the products of combustion cannot escape.

Another important aspect of a bomb calorimeter is that it is a closed system under pressure. In a bomb calorimeter, processes occur at constant volume but not constant pressure. Because the pressure can change significantly, the amount of heat transferred from the system to the calorimeter is not the same as the change in enthalpy of the system. If chemists want to find the enthalpy of a substance tested in a bomb calorimeter, they must make corrections to account for the change in pressure conditions. A correction factor is introduced into the calculations and the equation used is $Q = C\Delta T + RT\Delta n_{(\text{gas})}$. R is the universal gas constant and $\Delta n_{(\text{gas})}$ is the change in total moles of gas. However, for the purposes of the bomb calorimeter calculations you will perform, assume that the total moles of gas of reactants and products remains the same. As such, you can use the equation $Q = C\Delta T$. The following Sample Problem illustrates how to use the heat capacity of a bomb calorimeter in your calculations.

Sample Problem

Calculating Thermal Energy in a Bomb Calorimeter

Problem

A laboratory was contracted to test the energy content of a sample of peanut butter. A technician placed a 16.0 g sample of peanut butter in the steel bomb of a bomb calorimeter, along with sufficient oxygen to combust the sample completely. He ignited the mixture and took temperature measurements. The heat capacity of the calorimeter was previously determined to be $8.28 \text{ kJ}/^\circ\text{C}$. During the experiment, the temperature increased by 50.5°C .

- What was the amount of thermal energy released by the sample of peanut butter?
- How much heat was released per gram of the peanut butter combusted?



A chemist prepares a sample for testing in a bomb calorimeter.

What Is Required?

You need to calculate the thermal energy lost by the peanut butter.

You need to calculate the heat released per gram of peanut butter combusted.

What Is Given?

You know the mass of peanut butter, $m = 16.0 \text{ g}$

You know the heat capacity of the calorimeter, $C = 8.28 \text{ kJ}/^\circ\text{C}$

You know the change in temperature, $\Delta T = 50.5^\circ\text{C}$

| Plan Your Strategy | Act on Your Strategy |
|--|--|
| Calculate the amount of heat, Q , absorbed by the calorimeter. | $Q = C\Delta T$ $= \left(8.28 \frac{\text{kJ}}{^\circ\text{C}}\right)(50.5^\circ\text{C})$ $= 418.14 \text{ kJ}$ |
| Determine the amount of thermal energy released by the peanut butter sample, which is equal to the amount of heat, Q , absorbed by the calorimeter but opposite in sign. | $Q_{\text{peanut butter}} = -Q_{\text{calorimeter}}$ $= -418 \text{ kJ}$ |
| To find the heat released per gram, divide the amount of thermal energy released by the mass of the sample. | $\frac{Q}{m} = \frac{-418.14 \text{ kJ}}{16.0 \text{ g}}$ $= -26.1 \frac{\text{kJ}}{\text{g}}$ <p>The heat released per gram of peanut butter is 26.1 kJ/g.</p> |

Check Your Solution

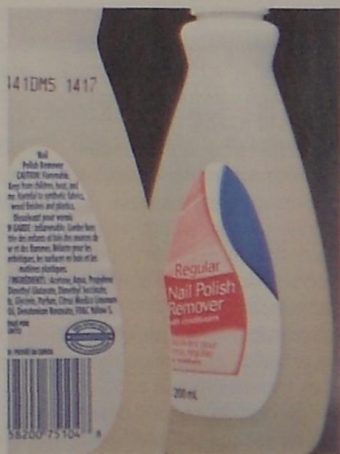
Thermal energy was released by the peanut butter, so it makes sense that the thermal energy value is negative.

Practice Problems

31. Predict the final temperature of a 5.00×10^2 g iron ring that is initially at 25.0°C and is heated by combusting 4.95 g of ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$; ΔH_{comb} for ethanol is -1234.8 kJ/mol. (Note: These are not standard conditions.)
32. Calculate the molar enthalpy of combustion of octane if 0.53 g of the fuel increased the temperature of a coffee can calorimeter (13 g of aluminum and 2.50×10^2 mL of water) by 17.2°C . Remember to include the heat gained by not only the water but also by the aluminum can.
33. How much propane (in grams) would have to be combusted to increase the temperature of 3.00×10^2 mL of water from 20.00°C to its boiling point? (The molar enthalpy of combustion of propane can be found in Table 5.4.)
34. A lab technician places a 5.00 g food sample into a bomb calorimeter with a heat capacity of 9.23 kJ/ $^\circ\text{C}$. The initial temperature of the calorimeter system is 21.0°C . After burning the food, the final temperature of the system is 32.0°C . How much thermal energy is released by the combustion of the food in kilojoules per gram?
35. Determine the enthalpy of combustion of an unknown fuel if a 2.75 g sample increased the temperature of 5.00×10^2 mL of hot chocolate ($c = 3.75$ J/g $^\circ\text{C}$) in a 1.50×10^2 g glass mug ($c = 0.84$ J/g $^\circ\text{C}$) from 10.00°C to 45.00°C . Express the value for enthalpy of combustion in appropriate units.
37. When a sample of ethene gas, $\text{C}_2\text{H}_4(\text{g})$, is burned the heat produced warms 50.0 g of water by 63.0°C . The mass of $\text{C}_2\text{H}_4(\text{g})$ burned was 0.268 g.
- What is the standard molar enthalpy of combustion for $\text{C}_2\text{H}_4(\text{g})$ in kilojoules per mole?
 - Write the thermochemical equation for this combustion reaction.
38. Diborane, $\text{B}_2\text{H}_6(\text{g})$, is a highly reactive compound that has been used as a reducing agent in rocket propellants. It can react with chlorine gas as written below.
- $$\text{B}_2\text{H}_6(\text{g}) + 6\text{Cl}_2(\text{g}) \rightarrow 3\text{BCl}_3(\text{g}) + 6\text{HCl}(\text{g}) + 755 \text{ kJ}$$
- A 2.85 g sample of $\text{B}_2\text{H}_6(\text{g})$ reacts with an excess of chlorine gas in a bomb calorimeter, which is calibrated to 8.82 kJ/ $^\circ\text{C}$. What change in temperature will occur when the sample reacts?
39. The equation below represents the burning of carbon disulfide, $\text{CS}_2(\ell)$, in a calorimeter. What mass of $\text{CS}_2(\ell)$ must have burned to increase the temperature of 1.00 kg of water by 15.5°C ?
- $$\text{CS}_2(\ell) + 3\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g}) + 1690 \text{ kJ}$$
40. A sample of acetone having a mass of 1.920 g undergoes complete combustion in an insulated calorimeter holding 400.0 mL of water. It is determined that the water and calorimeter together absorb 58.829 kJ of heat energy from this combustion. Based upon this information, what is the standard molar enthalpy of combustion for acetone in kilojoules per mole?



36. Urea, $\text{NH}_2\text{CONH}_2(\text{s})$, is widely used in various aspects of fertilizer manufacturing. A 4.28 g sample of urea is burned in a flame calorimeter. The calorimeter is made of aluminum and has a mass of 40.3 g. The 125.0 mL volume of water inside the calorimeter is at an initial temperature of 5.5°C . After the urea is completely combusted, the water temperature is 96.0°C . Use this information to calculate the enthalpy of combustion, ΔH_{comb} , for urea. Refer to Table 5.1 for the specific heat capacity of aluminum.



Acetone is a common ingredient in nail polish remover.

CANADIAN RESEARCH IN ACTION

Investigating the Thermodynamics of Aqueous Solutions



Dr. Hakin's research relies on techniques such as calorimetry to study the thermodynamics of aqueous systems.

Dr. Andrew Hakin, a professor at the Department of Chemistry and Biochemistry, University of Lethbridge, Alberta, is a world-renowned specialist in the field of experimental thermodynamics. "More specifically," he comments, "I specialize in utilizing techniques of calorimetry and densimetry to probe the thermodynamic properties of aqueous electrolyte systems." Dr. Hakin leads one of the few research groups in the world that take high-precision heat capacity measurements of aqueous solutions. In 2003, he received the Stig Sunner Memorial Award for his contributions to the field of calorimetry.

Dr. Hakin's team was one of the first to build a densimeter, a device that measures the properties of aqueous systems under high temperature and pressure. These measurements are critical in a number of different fields. One example is in designing nuclear power plants in which hot radioactive water is pumped at high pressure through thousands of metres of tubing. The radioactive water flowing through the tubes heats non-radioactive water on the outside of the tubes, producing steam that runs turbines to generate electricity. Engineers who design these tubes must understand the properties of radioactive water at high temperature and pressure.

Dr. Hakin's densimeter, which took about four years to build, can increase the temperature of an aqueous system to 523 K and the pressure exerted on it to 300 times atmospheric pressure. When Dr. Hakin and his team published results from their first experiment with the densimeter in 1998, they turned a long-held idea in the field of thermodynamics on its head. At the time, scientific models predicted that in aqueous solution, glycine—the most basic

of amino acids—would behave like a typical non-electrolyte when subjected to extreme temperature and pressure. Dr. Hakin's studies showed that under extreme temperature and pressure, glycine behaves not like a typical non-electrolyte, but more like a simple electrolyte, such as sodium chloride.

"We thought we had got it wrong, and so we repeated the experiment a number of times," recalls Dr. Hakin. "Eventually, we convinced ourselves that we were correct. It was a good achievement. We asked questions about some fundamental thermodynamic properties, designed an instrument [a densimeter] to achieve our goals, and got a result that made our community sit back and think."

In striving to find out whether he could verify the results of an accepted model with experimental data, Dr. Hakin discovered that he could not, and in the process made an important discovery. "Models are very useful and usually point us in the right direction, but there is no substitute for real experimental data," he explains. Other scientists have since repeated the experiment and achieved similar results, thus backing up Dr. Hakin's findings.

Related Career

Nuclear engineers design, develop, and maintain nuclear power plants. They must understand the processes that produce nuclear energy, including the properties of radiation and the science of thermodynamics. In Canada, many nuclear engineers have undergraduate degrees in engineering or science and graduate degrees in nuclear engineering.

QUESTIONS

1. How do the laws of thermodynamics provide the framework for the research that Dr. Hakin conducts into the properties of aqueous solutions at extreme temperature and pressure?
2. Use the Internet and/or print resources to assess the impact that the calorimeter has had on the study of thermodynamics.
3. Use Internet and/or print resources to find another career related to the research covered in this feature. Briefly describe the nature of this career and any training or education required.

Section Summary

- When a process takes place under conditions of constant pressure, the enthalpy change of a system is equal to the amount of heat gained or heat lost by the system.
- The standard enthalpy of a reaction as written (ΔH_r°) is the enthalpy change for the amount in moles of each reactant and product as determined by the coefficient of the term in the chemical equation.
- A process taking place in a simple calorimeter occurs at constant pressure. Therefore, the amount of heat that is exchanged between the calorimeter and the system is equal to the change in the enthalpy of the system.
- Temperature data from a simple calorimetry experiment can be used to calculate the enthalpy of a chemical reaction.
- The standard enthalpy of combustion ($\Delta H_{\text{comb}}^\circ$) of a compound is the enthalpy change that occurs when 1 mol of a compound reacts completely with oxygen under the conditions that the reactants started out at 25°C and 100 kPa of pressure and the products cooled to 25°C and 100 kPa of pressure after the reaction was complete.
- A process taking place in a bomb calorimeter occurs at constant volume but not constant pressure.

Review Questions

1. **(K/U)** What is the main characteristic of a calorimeter that allows you to determine the thermal energy change?
2. **(K/U)** Why is polystyrene a good material to make a simple calorimeter?
3. **(T/I)** A reaction in a calorimeter containing 80.0 g of water at 20.0°C causes the temperature to fall by 1.5°C. What is the thermal energy change of the water?
4. **(K/U)** The enthalpy of reaction for a neutralization reaction is to be determined by mixing dilute solutions of an acid and a base in a polystyrene coffee cup. What data must be recorded to complete this activity? What assumptions are made to complete the calorimetric calculations?
5. **(K/U)** In solving calorimetry problems, the assumption is usually made that the specific heat capacity of a dilute solution is equal to that of water. This is not a valid assumption for concentrated solutions. Suggest a reason why this assumption would not apply for concentrated solutions.
6. **(K/U)** The enthalpy change of a reaction, ΔH_r , that is calculated when a solid dissolves in water is -10.0 kJ/mol . Has the temperature of the water increased or decreased in this process? State a reason for your answer.
7. **(C)** You have learned about three types of calorimeters in this section. Use a Venn diagram to communicate the similarities and differences in these types of calorimeters. Include sources of error for each type of calorimeter in your summary.
8. **(A)** A chemist mixes 100.00 mL of 0.050 mol/L aqueous potassium hydroxide, KOH(aq) , with 100.00 mL of 0.050 mol/L nitric acid, $\text{HNO}_3\text{(aq)}$. The temperature of the reactants is 21.01°C. The temperature after the reaction is complete is 21.34°C.
 - a. Determine the molar enthalpy of neutralization for this reaction.
 - b. Write the thermochemical equation and draw an enthalpy diagram for the reaction.
9. **(C)** Calorimetry is based upon the first and second laws of thermodynamics. Explain this relationship in a brief paragraph supported by a diagram.
10. **(K/U)** A bomb calorimeter is classified as an isolated system because neither mass nor energy is exchanged with the surroundings. What type of system describes a flame calorimeter?
11. **(T/I)** A 6.60 g sample of a biscuit is burned in a bomb calorimeter having a heat capacity of 11.6 kJ/°C. After the burning is complete, the temperature has increased by 8.41°C. What amount of thermal energy was released per gram of biscuit?
12. **(A)** In order to study a person's energy expenditure and ability to burn different fuels such as carbohydrates or fats, a "whole-room calorimeter" is used. Research this topic and write a brief report that describes the design of the room and the measurements that must be taken.
13. **(K/U)** Provide an example of a thermochemical equation for a chemical reaction that requires energy to proceed. In your own words, describe how someone would read the equation.

Key Terms

Hess's law

standard molar enthalpy

of formation, ΔH_f°

thermal stability

Hess's law a law stating that the enthalpy change of a physical or chemical process depends only on the initial and final conditions of the process; the enthalpy change of the overall process is the sum of the enthalpy changes of its individual steps

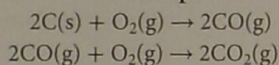
Many reactions release too much energy to be performed safely with a simple calorimeter. Also, simple calorimeters are usually used only for processes involving dilute aqueous solutions. In addition, many reactions occur too violently or too slowly for the calorimetric method to be practical. However, chemists can determine the enthalpy change of nearly any reaction by using some accumulated data and **Hess's law**, which is stated in the box below.

Hess's Law

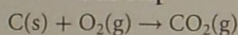
The enthalpy change of a physical or chemical process depends only on the initial and final conditions of the process. The enthalpy change of a multistep process is the sum of the enthalpy changes of its individual steps.

In 1840, Russian chemist Germain Henri Hess (1802–1850) stated the law that now bears his name. To understand Hess's law, analyze the example below, which shows that carbon dioxide can form from carbon and oxygen by one step or by two steps.

Two Steps



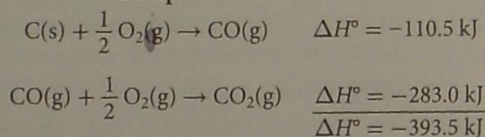
One Step



According to Hess's law, the sum of the enthalpy changes for the two reactions on the left should be the same as the enthalpy change for the single reaction on the right. However, notice that if you determine the enthalpy changes for the reactions on the left as written, you obtain the enthalpy change for the formation of 2 mol of carbon dioxide. The enthalpy change for the reaction on the right, as written, represents the formation of 1 mol of carbon dioxide. To compare the reactions, you must compare the same amount in moles of product. Therefore, you must divide the coefficients of the two reactions on the left by 2, as shown in the equations below under the title, Two Steps.

Keep in mind also that comparing enthalpy changes of chemical reactions requires carrying out the reactions under the same conditions. Chemists have agreed to use the standard enthalpy change, ΔH° , which implies conditions at SATP. For chemical reactions in solution, the standard state also includes a concentration of exactly 1 mol/L. Now you can compare the two pathways by which carbon dioxide could form from carbon and oxygen. Notice that the standard enthalpy change for the two pathways is the same. You can also represent this comparison with an enthalpy diagram, as shown in **Figure 5.20**.

Two Steps



One Step

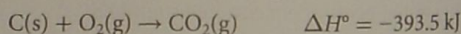
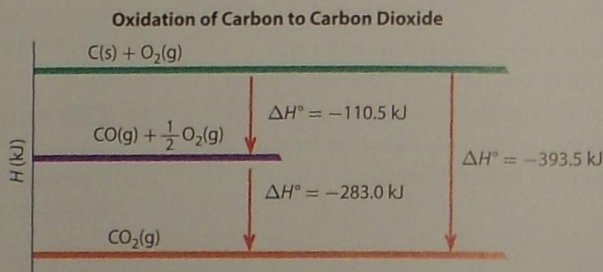


Figure 5.20 Carbon dioxide can be formed by the reaction of carbon with oxygen via two different pathways. The enthalpy change of the overall reaction is the same for either pathway.



Two Pathways, One Change

One way to think about Hess's law is to compare the energy changes that occur in a chemical reaction with the changes in the potential energy of a mountain biker on hilly terrain. This comparison is shown in **Figure 5.21**. Hess's law is valid because enthalpy change is determined only by the initial and final conditions of the system. It is not dependent on the pathway of the system. Hess's law allows you to calculate the enthalpy change of a chemical reaction when it is not practical to use a calorimeter to find the enthalpy change of a reaction. You can, however, use a calorimeter to find the enthalpy changes of other reactions. You can combine the equations of these reactions to arrive at the equation of the reaction in which you are interested.

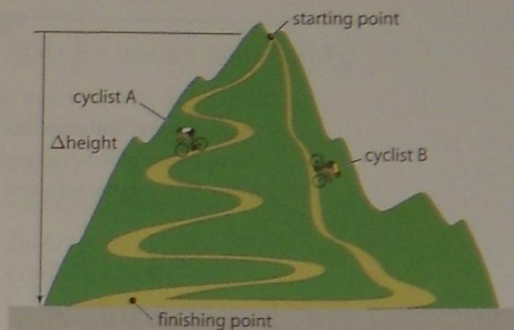


Figure 5.21 The routes that cyclists take to get from the starting point to the finishing point have no effect on the net change in the cyclists' gravitational potential energy. Similarly, enthalpy change is not dependent on the pathway of a system.

Combining Sets of Chemical Equations

You can use Hess's law to find the enthalpy change of any reaction as long as you know the enthalpy changes for any set of reactions that add up to the overall reaction in which you are interested. For example, the first two steps in the industrial synthesis of sulfuric acid are shown below and the entire process is depicted in **Figure 5.22**.

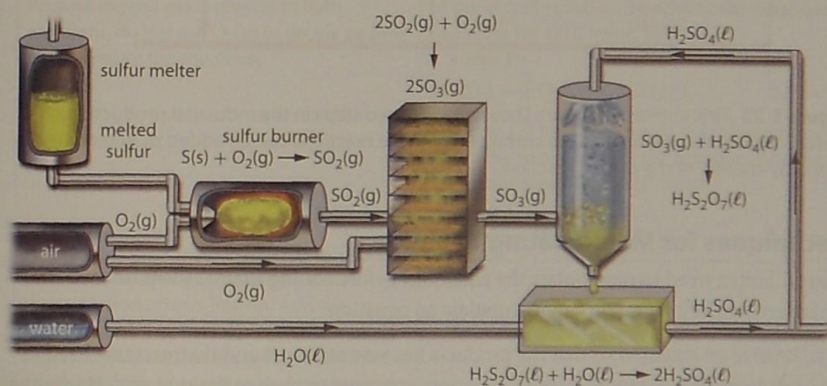
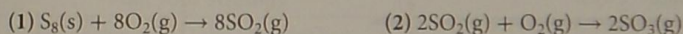
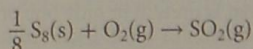
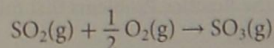


Figure 5.22 The industrial production of sulfuric acid shown here is called the contact process. The second step, the oxidation of sulfur dioxide, is very slow. Therefore, the system is designed to cause the gases to come in contact with a catalyst (illustrated by the box containing many layers), which speeds up the reaction.

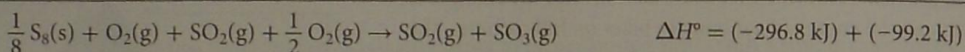
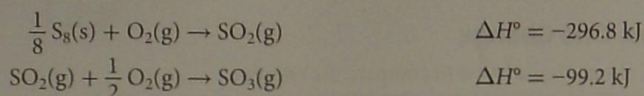
Suppose you want to find the enthalpy change for the formation of sulfur trioxide from sulfur and oxygen. You must examine the equations and decide whether you need to divide the coefficients by a constant. Because you want 1 mol of sulfur trioxide in the final step, you want only 1 mol of sulfur dioxide in the first step, thus you need to divide the first equation by 8.



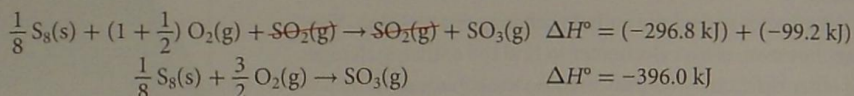
You must also divide the second equation by 2.



Write the two equations with their arrows aligned, write their known standard enthalpy changes beside the equations, and add the equations and the standard enthalpy changes.



Examine the final equation to find any compounds occurring on both sides. These compounds will cancel each other. Also, look for any compounds that occur more than once on the same side, and add them together.



The enthalpy diagram representing the process of synthesizing sulfur trioxide is shown in **Figure 5.23**.

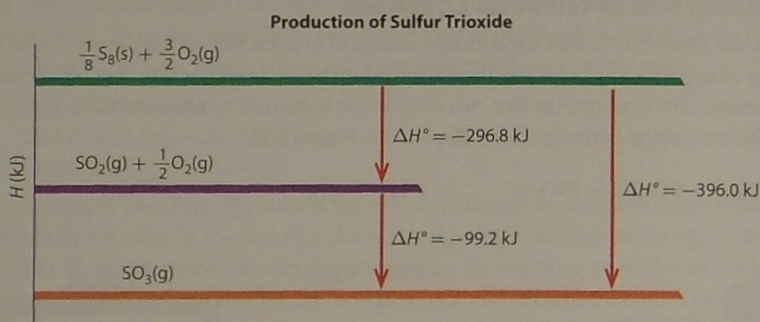


Figure 5.23 This enthalpy diagram shows the first two steps in the industrial production of sulfuric acid. It also shows that the enthalpies of these reactions can be added to determine the enthalpy change of the overall reaction.

Techniques for Manipulating Equations

You will often need to manipulate the equations before adding them, as was done above. There are two key ways you can manipulate an equation:

1. *Reverse an equation* so that the products become reactants and the reactants become products. When you reverse an equation, you need to change the sign of ΔH (multiply by -1). When a reaction is written in reverse, the enthalpy change has the opposite sign.
2. *Multiply each coefficient* in an equation by the same integer or fraction. When you multiply an equation, you need to multiply ΔH by the same number. Recall that the enthalpy change is directly related to the amount of the substances involved in a reaction. If two candles are burned instead of one, then twice as much heat and light will be produced.

When the same reactant or product is present in equations that you are manipulating, do not use that reactant or product to decide how to manipulate the equations. Always start with a reactant or product that is present in only one of the equations and that is also present in the overall equation.

Examine the following Sample Problem to see how to manipulate equations so that they add to the overall equation. Try the Practice Problems that follow to practise finding the enthalpy change by adding equations.

Suggested Investigation

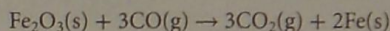
Inquiry Investigation 5-B,
Hess's Law and the
Enthalpy of Combustion
of Magnesium

Sample Problem

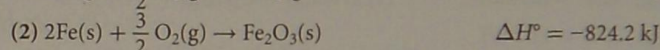
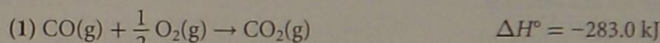
Using Hess's Law To Determine Enthalpy Change

Problem

One of the methods used in the steel industry to obtain metallic iron is to react iron(III) oxide, $\text{Fe}_2\text{O}_3(\text{s})$, with carbon monoxide, $\text{CO}(\text{g})$, as shown in the balanced equation below:



Determine the enthalpy change of this reaction, given the following equations and their enthalpy changes.



What Is Required?

You need determine the enthalpy change of a reaction by using two other reactions.

What Is Given?

You are given the overall equation and the two chemical equations and their corresponding enthalpy changes.

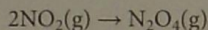
| Plan Your Strategy | Act on Your Strategy |
|--|---|
| Examine equations (1) and (2) to see how they compare with the overall equation. Because oxygen gas is present in both equations, do not use $\text{O}_2(\text{g})$ to decide on how to manipulate the equations. | Equation (1) has $\text{CO}(\text{g})$ as a reactant and $\text{CO}_2(\text{g})$ as a product, as does the overall equation. The stoichiometric coefficients do not match the coefficients of the overall equation. To achieve the same coefficients, multiply equation (1), including the ΔH° value, by 3. $3 \times \text{eq. (1):}$ $3\text{CO}(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) \quad \Delta H^\circ = 3(-283.0 \text{ kJ})$ Equation (2) has the required stoichiometric coefficients, but $\text{Fe}(\text{s})$ and $\text{Fe}_2\text{O}_3(\text{s})$ are on the wrong sides of the equation. Reverse equation (2) and, therefore, change the sign of the ΔH° value. $-1 \times \text{eq. (2):}$ $\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 2\text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \quad \Delta H^\circ = -1(-824.2 \text{ kJ})$ |
| Write the manipulated equations so that their equation arrows line up. Add the reactants and products on each side, and cancel substances that appear on both sides in equal amounts. Ensure that the manipulated equations add to the overall equation. | $ \begin{array}{r} 3\text{CO}(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) \\ \text{Fe}_2\text{O}_3(\text{s}) \rightarrow 2\text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \\ \hline 3\text{CO}(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) + \text{Fe}_2\text{O}_3(\text{s}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{Fe}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \\ \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{Fe}(\text{s}) \end{array} $ |
| Add the manipulated enthalpy values for the equations. | $ \begin{aligned} \Delta H^\circ &= 3(-283.0 \text{ kJ}) + (-1(-824.2 \text{ kJ})) \\ &= -849.0 \text{ kJ} + 824.2 \text{ kJ} \\ &= -24.8 \text{ kJ} \end{aligned} $ |
| Write the overall equation and enthalpy change. | $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{Fe}(\text{s}) \quad \Delta H^\circ = -24.8 \text{ kJ}$ |

Check Your Solution

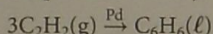
The equations added correctly to the overall equation. Check to ensure that you adjusted ΔH° accordingly for each equation. Because you added the ΔH° values, the final answer will be as precise as the least precise number used in the calculation. The final answer has one digit after the decimal point, which is correct.

Practice Problems

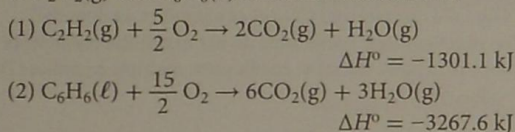
- 41.** Nitrogen dioxide, $\text{NO}_2(\text{g})$, is an emission resulting from the burning of gasoline in air in an automobile engine. Nitrogen dioxide contributes to the formation of smog and acid rain. It can be converted to dinitrogen tetroxide as shown below:



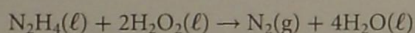
- a.** Use Hess's law and the following equations to determine the enthalpy change for this reaction.
- (1) $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H^\circ = 66.4 \text{ kJ}$
- (2) $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) \quad \Delta H^\circ = 11.1 \text{ kJ}$
- b.** Write the thermochemical equation for the overall reaction.
- 42.** Ethyne, $\text{C}_2\text{H}_2(\text{g})$, can be converted to benzene, $\text{C}_6\text{H}_6(\ell)$, over a palladium catalyst.



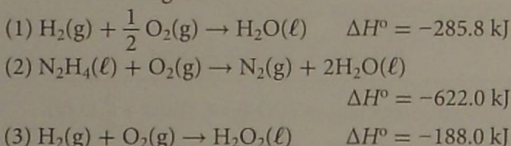
Determine the enthalpy of reaction for this process from the equations below that show the combustion of $\text{C}_2\text{H}_2(\text{g})$ and $\text{C}_6\text{H}_6(\ell)$ at standard conditions.



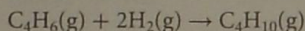
- 43.** Hydrazine, $\text{N}_2\text{H}_4(\ell)$, is a high-energy compound used as a rocket propellant. Use Hess's law to determine the enthalpy of reaction when this compound reacts as follows:



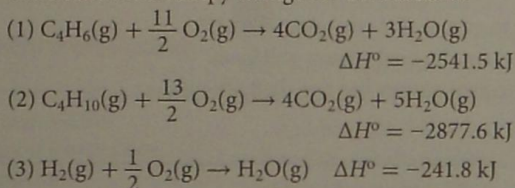
Use the following information:



- 44.** Synthetic rubber can be manufactured from the hydrocarbon buta-1,3-diene, $\text{C}_4\text{H}_6(\text{g})$. This compound reacts with hydrogen to produce butane, $\text{C}_4\text{H}_{10}(\text{g})$, as shown in the equation below:

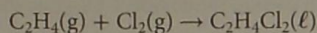


Use Hess's law and the equations that follow to determine the enthalpy change for this reaction.

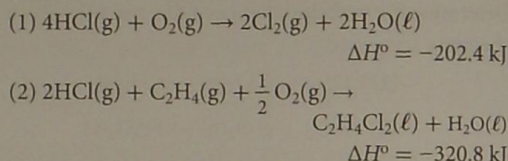


- 45.** Ethene, $\text{C}_2\text{H}_4(\text{g})$, is commonly used as an agent to hasten the ripening of fruit, such as bananas.

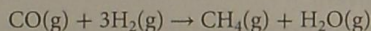
It can also be used to prepare 1,2-dichloroethane, $\text{C}_2\text{H}_4\text{Cl}_2(\ell)$, which is used to make vinyl chloride. Use Hess's law to determine the enthalpy of reaction for the preparation of $\text{C}_2\text{H}_4\text{Cl}_2(\ell)$.



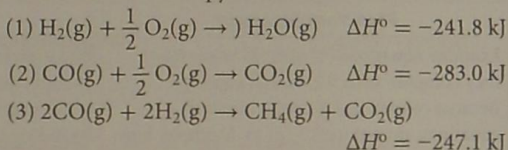
Given:



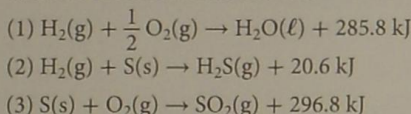
- 46.** Carbon monoxide, $\text{CO}(\text{g})$, can react with hydrogen, $\text{H}_2(\text{g})$, to produce methane, $\text{CH}_4(\text{g})$, and water vapour.



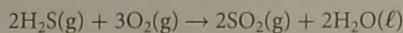
Given the following equations, use Hess's law to determine the enthalpy of reaction.



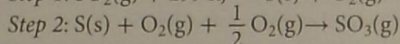
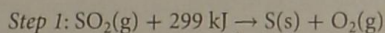
- 47.** The following thermodynamic equations have been obtained from reference sources:



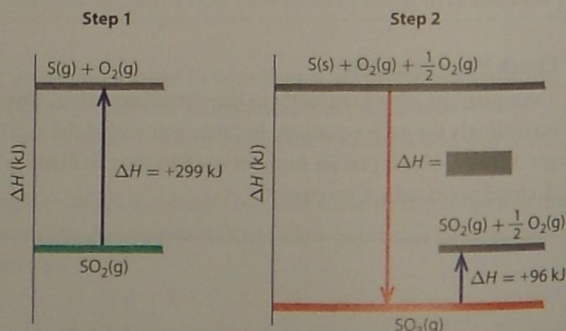
Use Hess's law to determine the enthalpy change for the reaction below:



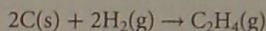
- 48.** The reaction to convert $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$ is a two-step process:



The enthalpy diagram below is a graphical representation of the process. Use this diagram to determine the enthalpy change for step 2.



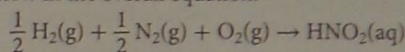
49. Ethene, $C_2H_4(g)$, is used in the manufacture of many polymers. If ethene could be formed from the elements carbon and hydrogen, the equation would be as follows:



Use Hess's law and the equations given below to determine the molar enthalpy of formation for $C_2H_4(g)$.

- (1) $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -393.5 \text{ kJ}$
 (2) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ = -285.8 \text{ kJ}$
 (3) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H^\circ = -1411.2 \text{ kJ}$

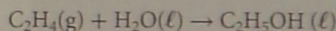
50. From the following equations, determine the molar enthalpy of formation for $HNO_2(aq)$, as shown below in the overall equation:



- (1) $NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l) \quad \Delta H^\circ = -320.1 \text{ kJ}$
 (2) $NH_3(aq) + HNO_2(aq) \rightarrow NH_4NO_2(aq) \quad \Delta H^\circ = -37.7 \text{ kJ}$
 (3) $2NH_3(aq) \rightarrow N_2(g) + 3H_2(g) \quad \Delta H^\circ = +169.9 \text{ kJ}$
 (4) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \quad \Delta H^\circ = -285.8 \text{ kJ}$

Learning Check

13. State Hess's law, and explain why it is useful.
 14. Under what standard conditions is ΔH° measured?
 15. What factor must be kept constant when comparing the enthalpy change between two reactions?
 16. Figure 5.20 shows an enthalpy diagram for the formation of $CO_2(g)$. Sketch an enthalpy diagram for the reverse process: the decomposition of $CO_2(g)$ to $C(s)$ and $O_2(g)$.
 17. How can data be obtained for the simpler steps that an overall reaction can take to apply Hess's law? For a reaction that can be represented by two or more simpler steps, must each step be experimentally carried out in order to use Hess's law? Explain your answer.
 18. What statement can be made that validates that the steps (the pathway) between initial reactants and final products do not affect enthalpy change?
 19. Use Hess's law to calculate the enthalpy of reaction for the reaction between ethene and water to form ethanol, as shown.



Use the enthalpies of combustion of ethene and ethanol shown below.

$$\Delta H_{\text{comb}}^\circ (C_2H_4(g)) = -1441.2 \text{ kJ}$$

$$\Delta H_{\text{comb}}^\circ (C_2H_5OH(l)) = -1366.8 \text{ kJ}$$

After completing the calculation, draw an enthalpy diagram for the reactions.

Standard Molar Enthalpies of Formation

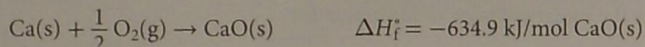
You have learned how to add equations for reactions with known standard enthalpy changes to find the enthalpy change of another reaction. Chemists have measured and calculated the standard enthalpy changes for thousands of chemical reactions. If you could find the right set of equations, you could calculate the standard enthalpy change for almost any reaction. How can you find these known enthalpy changes? Chemists have collected and organized data for one specific type of reaction that allow you to generate equations for almost any reaction. This type of reaction is a specific class of synthesis reaction in which the compound must be formed from its elements and not from any other compound.

The enthalpy change of formation for a compound at SATP is called the standard molar enthalpy of formation. The **standard molar enthalpy of formation, ΔH_f°** , is the change in enthalpy when 1 mol of a compound is formed directly from its elements in their most stable state at SATP (25°C and 100 kPa). Because elements in their most stable state have been selected as a reference, the standard enthalpy change of formation of the elements has been arbitrarily set at zero.

standard molar enthalpy of formation, ΔH_f° the change in enthalpy when 1 mol of a compound is formed directly from its elements in their most stable state at standard ambient temperature and pressure (SATP: 25°C and 100 kPa) and all solutions have a 1.0 mol/L concentration

Working with Standard Molar Enthalpies of Formation

Some molar enthalpies of formation are listed in **Table 5.5**. Additional molar enthalpies of formation are found in Appendix B. Notice that many of the formation equations include fractions. It is often necessary to use fractions in formation equations, because, by definition, they show the formation of exactly 1 mol of the product compound. For example, the following equation shows the formation of calcium oxide under standard conditions:



To produce 1 mol CaO(s), you need 1 mol Ca(s) and 0.5 mol O₂(g). If you were to eliminate the fractions by multiplying the coefficients by 2, the equation would show the formation of 2 mol CaO(s), not 1 mol.

Table 5.5 Selected Standard Molar Enthalpies of Formation

| Compound | Formation Equation | ΔH_f° (kJ/mol) |
|---|--|-----------------------------|
| CO(g) | $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ | -110.5 |
| CO ₂ (g) | $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ | -393.5 |
| CH ₄ (g) | $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$ | -74.6 |
| CH ₃ OH(l) | $\text{C(s)} + 2\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH(l)}$ | -239.2 |
| C ₂ H ₅ OH(l) | $2\text{C(s)} + 3\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH(l)}$ | -277.6 |
| C ₆ H ₆ (l) | $6\text{C(s)} + 3\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$ | +49.1 |
| C ₆ H ₁₂ O ₆ (s) | $6\text{C(s)} + 6\text{H}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ | -1273.3 |
| H ₂ O(l) | $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$ | -285.8 |
| H ₂ O(g) | $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(g)}$ | -241.8 |
| CaCl ₂ (s) | $\text{Ca(s)} + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$ | -795.4 |
| CaCO ₃ (s) | $\text{Ca(s)} + \text{C(s)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s})$ | -1207.6 |
| NaCl(s) | $\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)}$ | -411.2 |
| HCl(g) | $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl(g)}$ | -92.3 |
| HCl(aq) | $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl(aq)}$ | -167.5 |

Some elements exist in more than one form under standard conditions. For example, two forms of carbon are graphite and diamond, as shown in **Figure 5.24**. The enthalpy of formation of an element in its most stable state under standard conditions is arbitrarily set at zero. Graphite is the standard state of carbon. Therefore, the standard molar enthalpy of formation of graphite carbon is 0 kJ/mol. The standard molar enthalpy of formation of diamond is +1.9 kJ/mol.

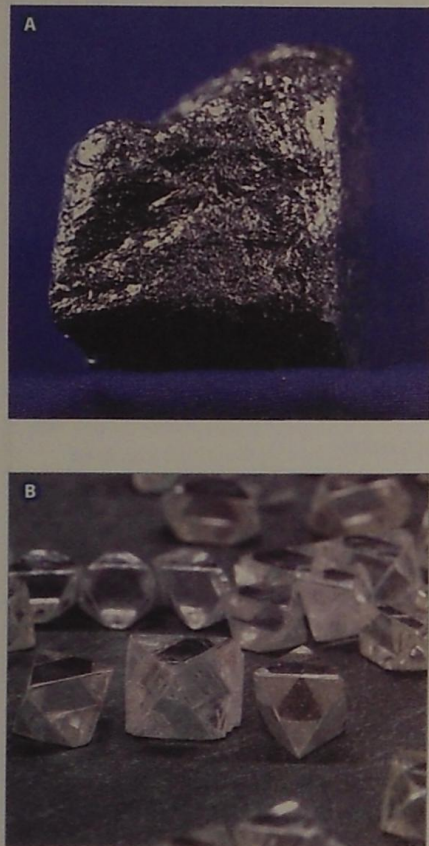


Figure 5.24 Two forms of carbon under standard conditions are graphite (**A**), used in pencil leads, and diamond (**B**). Carbon can, however, have only one standard state. Carbon's standard state is graphite.

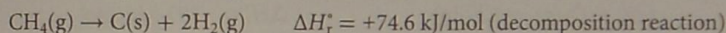
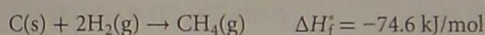
Analyze how you can use standard molar enthalpy of formation values to determine whether graphite or diamond is more stable at SATP.

Formation Reactions and Thermal Stability

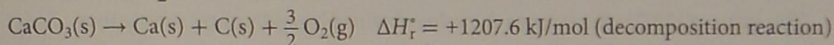
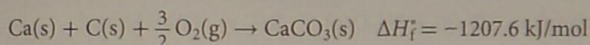
Formation reactions can provide information about how stable a substance is. The ability of a substance to resist decomposition when heated is known as its **thermal stability**. The reverse of a formation reaction is a decomposition reaction. The opposite sign of the enthalpy change of a formation reaction, therefore, is the enthalpy change of a decomposition reaction. The greater the enthalpy change of a decomposition reaction, the more energy input is required to decompose a substance into its elements. In other words, the greater the enthalpy change of a decomposition reaction, the greater is its thermal stability. For example, compare the enthalpies of decomposition of calcium carbonate, $\text{CaCO}_3(\text{s})$, and methane, $\text{CH}_4(\text{g})$. (Use the enthalpies of formation from **Table 5.5** and multiply by -1 .)

thermal stability the ability of a substance to resist decomposition when heated

- Methane's enthalpy of decomposition is $+74.6 \text{ kJ/mol}$.



- Calcium carbonate's enthalpy of decomposition is $+1207.6 \text{ kJ/mol}$.



Calcium carbonate requires a far greater energy input to decompose into its elements; therefore, calcium carbonate is considered more thermally stable.

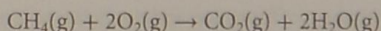
Using Enthalpies of Formation and Hess's Law

A variation of Hess's law allows you to calculate the enthalpy change of a chemical reaction by adding the enthalpies of formation of the products and subtracting the sum of the enthalpies of formation of the reactants. The following equation can be used to determine the enthalpy change of a chemical reaction:

$$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

where n represents the stoichiometric coefficient for each substance and Σ means "the sum of."

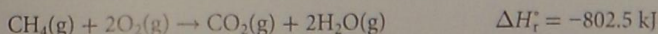
As usual, you need to begin with a balanced chemical equation. Consider, for example, the complete combustion of methane, $\text{CH}_4(\text{g})$:



Using the equation for the enthalpy change and the standard molar enthalpies of formation in Appendix B, you can calculate the enthalpy change for this reaction, as written.

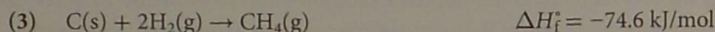
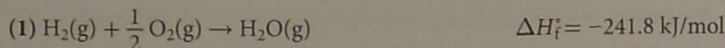
$$\begin{aligned}\Delta H_r^\circ &= \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants}) \\ &= [(1 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\text{g}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{CH}_4(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{O}_2(\text{g}))] \\ &= \left[(1 \text{ mol}) \left(-393.2 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol}) \left(-241.9 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol}) \left(-74.6 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol}) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] \\ &= (-877.1 \text{ kJ}) - (-74.6 \text{ kJ}) \\ &= -802.5 \text{ kJ}\end{aligned}$$

Note: Oxygen gas, $\text{O}_2(\text{g})$, at SATP is an element in its most stable state. Therefore, its standard enthalpy of formation is zero. Therefore,

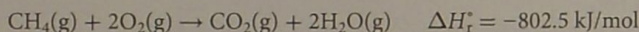
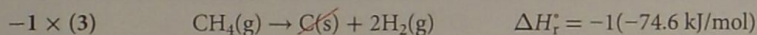
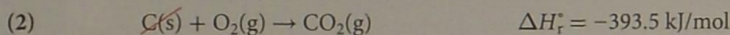
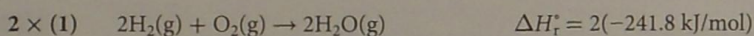


Relating Enthalpies of Formation and Hess's Law

Why does this method of adding and subtracting enthalpies of formation work, and how does this method relate to Hess's law? Consider the equations for the formation of each compound involved in the reaction of methane with oxygen:



There is no equation for the formation of oxygen, because oxygen is an element in its most stable state. By adding the formation equations and their enthalpy changes, you can obtain the overall equation. Notice that you must reverse equation (3) and multiply equation (1) by a factor of 2.



This value of ΔH_r° is the same as the value obtained by adding and subtracting enthalpies of formation. Therefore, using enthalpies of formation to determine the enthalpy of a reaction is consistent with Hess's law. In fact, using the formula in the box on the previous page makes it unnecessary to look for equations to add and carry out all of the extra steps. **Figure 5.25** shows the general process for determining the enthalpy of reaction from enthalpies of formation.

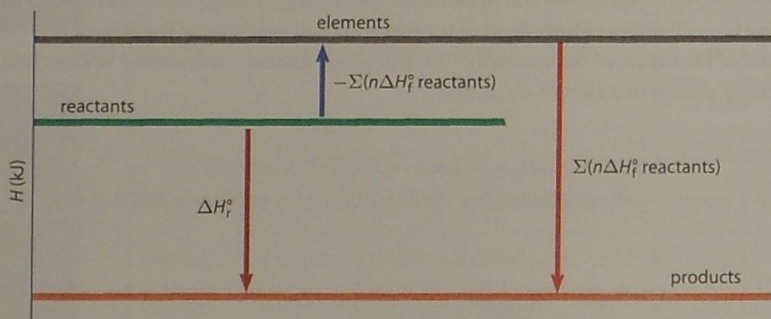


Figure 5.25 When using enthalpies of formation and Hess's law, you can visualize the overall reaction by imagining the reactants decomposing entirely into their elements and then the elements combining to form the products.

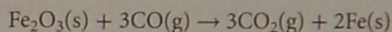
When using enthalpies of formation, remember that *the reactants do not actually break down into their elements and then react to form products*. Nevertheless, the method gives correct results because, according to Hess's law, the enthalpy change is the same, regardless of the pathway. The Sample Problem on the opposite page shows how to use enthalpies of formation to determine the enthalpy change of a reaction. Examine the second Sample Problem to learn how to determine enthalpy of formation using a known enthalpy of reaction. Then try the Practice Problems that follow.

Sample Problem

Using Enthalpies of Formation

Problem

Iron(III) oxide reacts with carbon monoxide to produce elemental iron and carbon dioxide. Determine the enthalpy change of this reaction by using known enthalpies of formation:



What Is Required?

You need to find ΔH_r° for the given chemical equation by using ΔH_f° data.

What Is Given?

From Appendix B, you can find the molar enthalpies of formation:

$$\Delta H_f^\circ \text{ of } \text{Fe}_2\text{O}_3(\text{s}) = -824.2 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{CO}(\text{g}) = -110.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{Fe}(\text{s}) = 0 \text{ kJ/mol (by definition, because Fe(s) is elemental iron in its most stable state)}$$



Iron ores are rocks that are rich in iron oxide and are an economical source of metallic iron.

Plan Your Strategy

Substitute the known values for enthalpies of formation into the equation:

$$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

Act on Your Strategy

$$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

$$= [(3 \text{ mol})(\Delta H_f^\circ \text{ CO}_2(\text{g})) + (2 \text{ mol})(\Delta H_f^\circ \text{ Fe}(\text{s}))] - [(1 \text{ mol})(\Delta H_f^\circ \text{ Fe}_2\text{O}_3(\text{s})) + (3 \text{ mol})(\Delta H_f^\circ \text{ CO}(\text{g}))]$$

$$= \left[(3 \text{ mol}) \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol}) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol}) \left(-824.2 \frac{\text{kJ}}{\text{mol}} \right) + (3 \text{ mol}) \left(-110.5 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$= (-1180.5 \text{ kJ} + 0 \text{ kJ}) - (-824.2 \text{ kJ} - 331.5 \text{ kJ})$$

$$= -1180.5 \text{ kJ} + 1155.7 \text{ kJ}$$

$$= -24.8 \text{ kJ}$$

$$\text{Therefore, } \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{Fe}(\text{s}) \quad \Delta H_r^\circ = -24.8 \text{ kJ}$$

Check Your Solution

A balanced chemical equation was used in the calculation. The answer is correctly expressed to the same precision as ΔH_f° , with one digit after the decimal point. The units are also correct.

Sample Problem

Using an Enthalpy of Combustion to Determine an Enthalpy of Formation

Problem

Octane, $\text{C}_8\text{H}_{18}(\ell)$, one of the major components in gasoline, burns completely with oxygen, producing carbon dioxide and water vapour. The molar enthalpy of combustion of octane in these conditions is -5074.1 kJ/mol . Determine the molar enthalpy of formation of octane.

What Is Required?

You need to write a balanced chemical equation for the reaction. You need to find ΔH_f° of octane by using the given molar enthalpy of combustion for octane and ΔH_f° data.

What Is Given?

$$\Delta H_{\text{comb}}^\circ \text{ of } \text{C}_8\text{H}_{18}(\ell) = -5074.1 \text{ kJ/mol}$$

From Appendix B, you can obtain the molar enthalpies of formation.

$$\Delta H_f^\circ \text{ of } \text{O}_2(\text{g}) = 0 \text{ kJ/mol (by definition)}$$

$$\Delta H_f^\circ \text{ of } \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$$

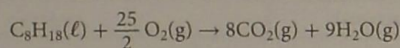
$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O}(\text{g}) = -241.8 \text{ kJ/mol}$$

Plan Your Strategy

- Write a chemical equation representing the combustion of octane in an open system.
- Use the available ΔH_f° data and the $\Delta H_{\text{comb}}^\circ$ (enthalpy of combustion of octane) to substitute into the equation $\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$, multiplying by the molar coefficients.
- Solve for the unknown ΔH_f° for octane.

Act on Your Strategy

- Write and balance the chemical equation for the combustion of 1 mol of octane:



- (Note: The overall reaction is a combustion reaction, so use $\Delta H_{\text{comb}}^\circ$ for ΔH_r° .)

$$\begin{aligned} \Delta H_r^\circ &= \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants}) \\ \Delta H_{\text{comb}}^\circ \text{ C}_8\text{H}_{18}(\ell) &= \left[(8 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (9 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\text{g})) \right] - \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_8\text{H}_{18}(\ell)) + \left(\frac{25}{2} \text{ mol} \right) (\Delta H_f^\circ \text{O}_2(\text{g})) \right] \\ -5074.1 \text{ kJ} &= \left[(8 \text{ mol}) \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) + (9 \text{ mol}) \left(-241.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_8\text{H}_{18}(\ell)) + \left(\frac{25}{2} \text{ mol} \right) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] \\ -5074.1 \text{ kJ} &= (-3148.0 \text{ kJ} - 2176.2 \text{ kJ}) - (1 \text{ mol})(\Delta H_f^\circ \text{C}_8\text{H}_{18}(\ell)) \end{aligned}$$

- $(1 \text{ mol})(\Delta H_f^\circ \text{C}_8\text{H}_{18}(\ell)) = +5074.1 \text{ kJ} - 3148.0 \text{ kJ} - 2176.2 \text{ kJ}$

$$\begin{aligned} \Delta H_f^\circ \text{ C}_8\text{H}_{18}(\ell) &= \frac{-250.1 \text{ kJ}}{1 \text{ mol}} \\ &= -250.1 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

The enthalpy of formation of octane, $\text{C}_8\text{H}_{18}(\ell)$, is -250.1 kJ/mol .

Check Your Solution

A balanced chemical equation was used in the calculation with appropriate molar coefficients. The answer is and should be expressed to the same precision as ΔH_f° , with one digit after the decimal point. The units are also correct.

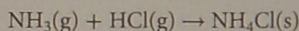
Practice Problems

Refer to Appendix B for data on molar enthalpies of formation.

51. The complete combustion of ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$, yields carbon dioxide and water vapour.

- Write the balanced chemical equation for this reaction.
- Use enthalpies of formation to determine the enthalpy of combustion, $\Delta H_{\text{comb}}^\circ$, in kilojoules per mole of $\text{C}_2\text{H}_5\text{OH}(\ell)$.

52. A reagent bottle containing concentrated aqueous ammonia, $\text{NH}_3(\text{aq})$, is accidentally left open near a bottle of concentrated hydrochloric acid, $\text{HCl}(\text{aq})$. The cloud of white smoke that forms in the air near the two containers is ammonium chloride, $\text{NH}_4\text{Cl}(\text{s})$. The following reaction occurs in the air:



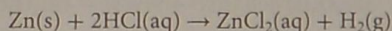
Use the standard molar enthalpies of formation to calculate the enthalpy of reaction.

53. A piece of zinc reacts completely with hydrochloric acid, $\text{HCl}(\text{aq})$, to produce an aqueous solution of zinc chloride, $\text{ZnCl}_2(\text{aq})$, and hydrogen gas.

- Use the data shown below to determine the enthalpy of reaction per mole of zinc.

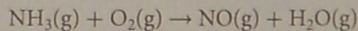
$$\Delta H_f^\circ \text{ of } \text{HCl}(\text{aq}) = -167.2 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{ZnCl}_2(\text{aq}) = -488.2 \text{ kJ/mol}$$



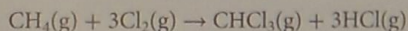
- What mass of zinc must be used for 123 kJ of heat to be given off?

54. Ammonia reacts with oxygen according to the following unbalanced equation:



Use standard molar enthalpies of formation to find the enthalpy of reaction for this reaction.

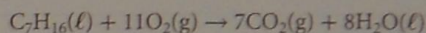
55. Consider the following equation representing the reaction of methane and chlorine to form chloroform, $\text{CHCl}_3(\text{g})$:



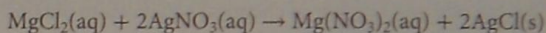
$$\Delta H^\circ = -305.0 \text{ kJ}$$

Use standard molar enthalpies of formation to determine the molar enthalpy of formation for chloroform.

56. The molar enthalpy of combustion for heptane, $\text{C}_7\text{H}_{16}(\ell)$, in a bomb calorimeter is -4816.7 kJ/mol of heptane. Using this and ΔH_f° data, determine the molar enthalpy of formation of heptane.



57. A double displacement reaction occurs when solutions of magnesium chloride, $\text{MgCl}_2(\text{aq})$, and silver nitrate, $\text{AgNO}_3(\text{aq})$, are mixed. Assume that the reaction goes to completion and that all of the silver chloride that forms precipitates as $\text{AgCl}(\text{s})$.



Use the given enthalpy of formation data to determine the enthalpy of reaction.

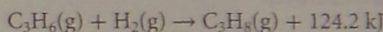
$$\Delta H_f^\circ \text{ of } \text{MgCl}_2(\text{aq}) = -801.2 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{Mg}(\text{NO}_3)_2(\text{aq}) = -881.6 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{AgCl}(\text{s}) = -127.0 \text{ kJ/mol}$$

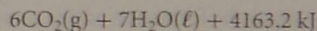
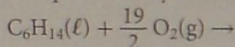
$$\Delta H_f^\circ \text{ of } \text{AgNO}_3(\text{aq}) = -101.8 \text{ kJ/mol}$$

58. Hydrogen gas reacts with propene gas, $\text{C}_3\text{H}_6(\text{g})$, in an addition reaction to produce propane, $\text{C}_3\text{H}_8(\text{g})$.

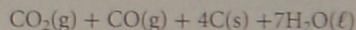
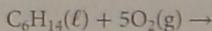


Use enthalpy of formation data and the information given in the above equation to determine the enthalpy of formation of propene.

59. The complete combustion of hexane, $\text{C}_6\text{H}_{14}(\ell)$, can be represented by the following equation:

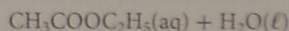
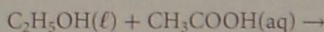


One possible reaction for the incomplete combustion of $\text{C}_6\text{H}_{14}(\ell)$ is as follows:



Determine the amount of energy lost per mole of $\text{C}_6\text{H}_{14}(\ell)$ when combustion is incomplete as written. The standard molar enthalpy of formation for $\text{C}_6\text{H}_{14}(\ell)$ is -198.7 kJ/mol .

60. Ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$, reacts with a 1.00 mol/L solution of acetic acid to produce ethyl ethanoate, a solvent used to make protective coatings such as polyurethane.



Calorimetry experiments determine that the enthalpy of reaction is 43 kJ. Use this information and the enthalpy of formation data to calculate the enthalpy of formation of ethyl ethanoate. The enthalpy of formation for 1.00 mol/L $\text{CH}_3\text{COOH}(\text{aq})$ is -486.0 kJ/mol .

Section Summary

- Hess's law states that the enthalpy change of a physical or chemical process depends only on the initial and final conditions. The enthalpy change of the overall process is the sum of the enthalpy changes of its individual steps.
- You can add any number of chemical equations to obtain an equation that you need, and the enthalpy change of the overall reaction is the sum of the enthalpy changes of the individual reactions.
- You can manipulate chemical equations to make them fit into another set of reactions by multiplying the equation by a constant or by reversing the equation. If you multiply by a constant, you must multiply the enthalpy change by that same constant. If you reverse an equation, you must change the sign of the enthalpy change.
- The standard enthalpy of formation of a compound (ΔH_f°) is the enthalpy change for the formation of 1 mol of the compound from its elements in their most stable state under standard conditions.
- The enthalpy of formation of an element in its most stable state under standard conditions is arbitrarily set at zero.
- You can calculate the enthalpy change for any reaction by applying the formula

$$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

Review Questions

- K/U** What is the difference between the standard molar enthalpy of formation for a compound and the standard enthalpy change for a reaction in which that compound is a product?
- T/I** The standard molar enthalpy of formation for ammonium hydrogen carbonate, $(\text{NH}_4)\text{HCO}_3(\text{s})$, is -849.4 kJ/mol . Write the thermochemical equation to show the formation of this compound.
- T/I** The standard molar enthalpy of formation of sulfuric acid, $\text{H}_2\text{SO}_4(\text{l})$, is -814.0 kJ/mol . The standard state for sulfur is orthorhombic sulfur, $\text{S}_8(\text{s})$. Write the thermochemical equation to represent the enthalpy of formation for $\text{H}_2\text{SO}_4(\text{l})$.
- A** Use Hess's law and the equations shown below to determine the enthalpy of reaction for

$$2\text{NOCl}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g})$$

$$(1) \frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) \quad \Delta H^\circ = +90.5 \text{ kJ}$$

$$(2) \text{NO}(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NOCl}(\text{g}) \quad \Delta H^\circ = -39.0 \text{ kJ}$$
- T/I** Use the given information and Hess's law to show how the enthalpy of reaction can be determined for the following reaction:

$$\text{P}_4\text{O}_{10}(\text{s}) + 6\text{PCl}_5(\text{s}) \rightarrow 10\text{Cl}_3\text{PO}(\text{g})$$

$$(1) \text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_3(\text{l}) \quad \Delta H^\circ = -1272 \text{ kJ}$$

$$(2) \text{P}_4(\text{s}) + 5\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s}) \quad \Delta H^\circ = -2915 \text{ kJ}$$

$$(3) \text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{s}) \quad \Delta H^\circ = -125 \text{ kJ}$$

$$(4) \text{PCl}_3(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{Cl}_3\text{PO}(\text{g}) \quad \Delta H^\circ = -267 \text{ kJ}$$
- T/I** 21.9 kJ of energy is released when 5.48 g of barium is oxidized to barium oxide, $\text{BaO}(\text{s})$. What is the enthalpy of formation of $\text{BaO}(\text{s})$?

$$\text{Ba}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{BaO}(\text{s})$$
- K/U** The standard molar enthalpy of formation for oxygen gas, $\text{O}_2(\text{g})$, is zero. The enthalpy of formation for atomic oxygen, $\text{O}(\text{g})$, is $+250 \text{ kJ/mol}$. Why is there a difference in these values?
- T/I** Arrange the following compounds in decreasing order of thermal stability, and explain the basis for determining thermal stability: $\text{CrCl}_3(\text{s})$, $\text{CaCl}_2(\text{s})$, $\text{AgCl}(\text{s})$, $\text{NaCl}(\text{s})$.
- A** Consider the process below.

$$3\text{Fe}_3\text{O}_4(\text{s}) + 8\text{Al}(\text{s}) \rightarrow 9\text{Fe}(\text{s}) + 4\text{Al}_2\text{O}_3(\text{s})$$
 - What is the enthalpy of reaction for this process?
 - What amount of heat would be released when $1.000 \times 10^3 \text{ kg}$ of iron is produced?
- C** Refer to the enthalpy of formation of hydrazine, $\text{N}_2\text{H}_4(\text{l})$, in Appendix B. Would you expect this to be a thermally stable compound? Write your answer as an e-mail to a classmate who does not understand the concept.
- T/I** Use the enthalpy of formation data in Appendix B to determine the enthalpy of formation for chlorine trifluoride, $\text{ClF}_3(\text{g})$.

$$2\text{ClF}_3(\text{g}) + 2\text{NH}_3(\text{g}) \rightarrow$$

$$\text{N}_2(\text{g}) + 6\text{HF}(\text{g}) + \text{Cl}_2(\text{g}) + 1.200 \times 10^3 \text{ kJ}$$
- C** As your part of a group presentation to the class, prepare a discussion that includes an enthalpy diagram that explains the significance of a positive sign for the enthalpy of formation for a compound.
- A** How much heat is required to decompose 500.0 g of calcium carbonate, $\text{CaCO}_3(\text{s})$, into calcium oxide, $\text{CaO}(\text{s})$, and carbon dioxide?

$$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

SECTION 5.4

Energy Efficiency and Energy Resources

In the context of energy transfer and transformations, **efficiency** is the ratio of useful energy produced (*energy output*) to energy used in its production (*energy input*), expressed as a percentage. This definition can be expressed mathematically as shown in the box below. When you use this definition, however, you need to be clear about what you mean by “energy used.” **Figure 5.26** shows factors to consider when calculating efficiency or analyzing efficiency data.

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

Energy output

- energy delivered to consumer in usable form
- actual work done
- calculate using $Q = mc\Delta t$, $\Delta H = n\Delta H_x$

Note: x can be f, comb, r, vap, or melt

Energy input

- ideal energy content of fuel
- energy used to extract and transport fuel
- solar energy used to create fuel (e.g., biomass)
- energy used to build and maintain power plant
- calculate using Hess's law and $\Delta H = n\Delta H_x$

Key Terms

efficiency

heat content

efficiency the ratio of useful energy produced (energy output) to energy used in its production (energy input), expressed as a percentage

Figure 5.26 Efficiency is expressed as a percentage. Always specify what is included in the “energy input” part of the ratio.

It is often difficult to determine how much energy is used and exactly how much useful energy is produced. For example, consider the preparation of the meal shown in **Figure 5.27**. Should you include the fuel used in the transportation of the vegetables and meat to market? Should you include the fuel used by the farmer in his tractors to plow, plant, fertilize, and harvest the vegetables? What about the energy used to heat the stove to cook the meat and vegetables? What do you include when calculating the energy efficiency of a process?



Figure 5.27 This is a healthy meal, but how much energy was used to prepare it?

Often, an efficiency percentage only takes into account the energy output of a system, based on the theoretical energy content of the fuel. The efficiency of a thermal energy conversion (heating) system is often calculated by using calorimetry data (energy output) and a calculation for energy input, which is a theoretical quantity (usually determined by Hess's law). The energy output takes into account only the useful energy for a particular process. The energy input includes that energy plus all of the “wasted” energy that is used to heat the oven, the air in the oven, and the kitchen. Examine the following Sample Problem to learn how to determine energy efficiency. Try the Practice Problems that follow to practise calculating efficiency.

Sample Problem

The Efficiency of a Propane Barbecue

Problem

Propane, $\text{C}_3\text{H}_8(\text{g})$, is a commonly used barbecue fuel. Determine the efficiency of the barbecue as a heating device if 5.10 g of propane is required to change the temperature of 250.0 g of water contained in a 500.0 g stainless steel pot ($c = 0.503 \text{ J/g}\cdot^\circ\text{C}$) from 25.0°C to 75.0°C .

What Is Required?

You need to find the amount of energy released by the combustion of the propane.

You need to find how much energy was absorbed by the water and the pot.

You then need to use those values to determine the efficiency of the barbecue.

What Is Given?

$$m_{\text{propane used}} = 5.10 \text{ g}$$

$$c_{\text{stainless steel}} = 0.503 \text{ J/g}\cdot^\circ\text{C}$$

$$m_{\text{water}} = 250.0 \text{ g}$$

$$\text{Initial temperature, } T_{\text{initial}} = 25.0^\circ\text{C}$$

$$m_{\text{steel pot}} = 500.0 \text{ g}$$

$$\text{Final temperature, } T_{\text{final}} = 75.0^\circ\text{C}$$

$$c_{\text{water}} = 4.19 \text{ J/g}\cdot^\circ\text{C}$$

Plan Your Strategy

Energy input

- Write a balanced chemical equation for the complete combustion of propane, and calculate ΔH_{comb}^* by using enthalpies of formation.
- Calculate the amount in moles of propane combusted from the mass and determine the theoretical energy content of the fuel.

Energy output

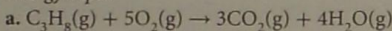
- Determine how much energy was absorbed by the pot and the water by using $Q = mc\Delta T$.

Efficiency

- Calculate the efficiency.

Act on Your Strategy

Energy input



$$\Delta H_{\text{comb}}^* = \Sigma(n\Delta H_f^* \text{ products}) - \Sigma(n\Delta H_f^* \text{ reactants})$$

$$= [(3 \text{ mol})(\Delta H_f^* \text{ CO}_2(\text{g})) + (4 \text{ mol})(\Delta H_f^* \text{ H}_2\text{O}(\text{g}))] - [(1 \text{ mol})(\Delta H_f^* \text{ C}_3\text{H}_8(\text{g})) + (5 \text{ mol})(\Delta H_f^* \text{ O}_2(\text{g}))]$$

$$= \left[(3 \text{ mol}) \left(-393.5 \frac{\text{kJ}}{\text{mol}} \right) + (4 \text{ mol}) \left(-241.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol}) \left(-103.8 \frac{\text{kJ}}{\text{mol}} \right) + (5 \text{ mol}) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$= -2043.9 \text{ kJ}$$

Therefore, the molar enthalpy of combustion of propane is $\Delta H_{\text{comb}}^* = -2043.9 \text{ kJ/mol}$.

- The amount in moles of $\text{C}_3\text{H}_8(\text{g})$ combusted is

$$n = \frac{m}{M}$$

$$= \frac{5.10 \text{ g}}{44.11 \frac{\text{g}}{\text{mol}}}$$

$$= 0.11562 \text{ mol}$$

Therefore, the energy content of the propane is

$$\Delta H = n\Delta H_{\text{comb}}^*$$

$$= (0.11562 \text{ mol}) \left(-2043.9 \frac{\text{kJ}}{\text{mol}} \right)$$

$$= -236 \text{ kJ}$$

Energy output

$$\begin{aligned} \text{c. } Q_{\text{total}} &= Q_{\text{water}} + Q_{\text{steel}} \\ &= mc\Delta T_{\text{water}} + mc\Delta T_{\text{steel}} \\ &= (250.0 \text{ g}) \left(4.19 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (75.0^\circ\text{C} - 25.0^\circ\text{C}) + (500.0 \text{ g}) \left(0.503 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (75.0^\circ\text{C} - 25.0^\circ\text{C}) \\ &= 6.50 \times 10^4 \text{ J} \\ &= 65.0 \text{ kJ} \end{aligned}$$

Efficiency

$$\begin{aligned} \text{d. efficiency} &= \frac{\text{energy output}}{\text{energy input}} \times 100\% \\ &= \frac{65.0 \text{ kJ}}{236 \text{ kJ}} \times 100\% \\ &= 27.5\% \end{aligned}$$

As a heating device, the barbecue was 27.5% efficient.

Check Your Solution

The units are correct. The efficiency is significantly less than 100%, which makes sense. Much of the thermal energy is transferred to the surrounding air and to the barbecue itself, rather than to the pot and to the water being heated.

Practice Problems

61. Using the data for the molar enthalpy of combustion of butane from **Table 5.4**, determine the efficiency of a lighter as a heating device if 0.70 g of butane is required to increase the temperature of a 250.0 g stainless steel spoon ($c = 0.503 \text{ J/g} \cdot ^\circ\text{C}$) by 45.0°C .
62. A solid camping fuel has a stated energy content of 50.0 kJ/g . Determine its efficiency if a 2.50 g piece of the fuel was required to increase the temperature of 500.0 g of soup ($c = 3.77 \text{ J/g} \cdot ^\circ\text{C}$) in a 50.0 g aluminum pot by 45.0°C .
63. Determine the efficiency of a heating device that burns methanol, $\text{CH}_3\text{OH}(\ell)$, given the following information:
- Data for Determining the Efficiency of a Methanol-burning Heater**
- | Quantity Being Measured | Data |
|--|-------------------------|
| Initial mass of burner | 38.37 g |
| Final mass of burner | 36.92 g |
| Mass of aluminum can | 257.36 g |
| Mass of aluminum can and water | 437.26 g |
| Initial temperature of water | 10.45°C |
| Final temperature of water | 23.36°C |
| $\Delta H_{\text{comb}}^{\circ}(\text{CH}_3\text{OH})$ | -726.1 kJ/mol |
64. What mass of pentane, $\text{C}_5\text{H}_{12}(\text{g})$, would have to be burned in an open system to heat $2.50 \times 10^2 \text{ g}$ of hot chocolate ($c = 3.59 \text{ J/g} \cdot ^\circ\text{C}$) from 20.0°C to 39.8°C if the energy conversion is 45.0% efficient?
65. Heat from burning a fuel is absorbed by a copper calorimeter. The calorimeter has a mass of 81.34 g and contains 200.00 g of water initially at 21.00°C .
- How much heat was absorbed by the calorimeter and the water if the final temperature of the water is 36.40°C ? Refer to **Table 5.1** for the required specific heat capacities.
 - The absorption of heat by the system is 45.00% efficient. How much heat was lost to the surroundings?
66. A furnace outputs $5.000 \times 10^4 \text{ kJ}$ of heat to an empty room. The following information is given:
- dimensions of room: $10.0 \text{ m} \times 10.0 \text{ m} \times 10.0 \text{ m}$
density of air: 1.290 kg/m^3
specific heat capacity of air: $1.01 \text{ J/g} \cdot ^\circ\text{C}$
initial air temperature: 12.0°C
final air temperature: 26.0°C
- Calculate the quantity of heat gained by the air in this room.
 - Determine how much heat was lost from the room, and calculate an efficiency rating for the retention of heat for this room.

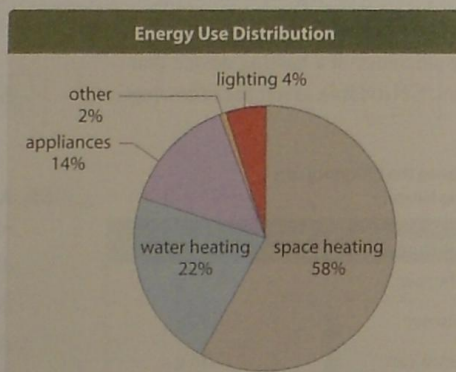
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67. A steel steam boiler has a mass of 1.50×10^3 kg and contains 255.00 kg of water at 35.00°C . Heat absorption by the boiler is 75.45% efficient. How much heat is required to increase the temperature of the system to the boiling point of water? The specific heat capacity of steel is $0.488 \text{ J/g}\cdot^\circ\text{C}$. The answer may be expressed in megajoules ($1 \text{ MJ} = 1 \times 10^6 \text{ J}$).
68. A flame calorimeter is used to determine the heat content of wood. The aluminum can in the apparatus has a mass of 180.51 g and holds 1.000 kg of water initially at 15.6°C . After 5.50 g of wood is burned, the water temperature increases to 20.7°C .
- Calculate the energy output that is absorbed by the calorimeter and the water.
 - An estimate of the recoverable heat content for the wood is 6.5 kJ/g . How much heat could be available in the sample of wood?
 - Determine the efficiency of the system in measuring the heat content of the wood.
69. Refer to **Tables 5.3 and 5.4** to obtain data necessary for the following questions.
- What mass of methane must burn to warm 60.00 g of water from 25.0°C to its boiling point and then turn it into steam at 100.0°C ? (**Hint:** Two steps are involved: warming of the water to 100.0°C , and then change of the liquid water to a vapour at 100.0°C).
 - If the transfer of heat is 56.5% efficient, what quantity of heat must come from the burning of methane?
 - What mass of methane must be burned at this efficiency rating?
70. Ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$, is used as a fuel in an alcohol burner. A glass beaker that has a mass of 386.00 g and a specific heat capacity of $0.880 \text{ J/g}\cdot^\circ\text{C}$ is filled with 125.00 g of water initially at 15.5°C . The beaker of water is placed next to the burner. When 1.24 g of ethanol burns, the water temperature in the beaker increases to 48.7°C . What is the efficiency of the transfer of heat to the beaker and the water? The enthalpy of combustion of ethanol is 1366.8 kJ/mol .

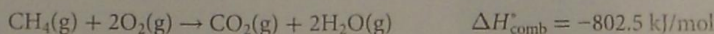
Using Energy Efficiently

Figure 5.28 summarizes energy use in Canadian homes by category. Canadians also use a great deal of energy getting from place to place. Forms of transportation account for 25 percent of all energy use. According to the first law of thermodynamics, energy is not destroyed, only transformed. You also know, from the second law of thermodynamics, that no process is completely efficient. Therefore, the challenge in developing more efficient technology is to find ways to convert more of the input energy into a useful form.

Figure 5.28 Most of the energy used in Canadian homes is for heating.



When assessing the efficiency of appliances, manufacturers focus on a single energy conversion—the input of electrical energy versus the output of useful energy. When looking at the bigger picture of energy efficiency, you also need to think about the source of the electricity. Consider, for example, natural gas. Natural gas is primarily methane. Therefore, you can estimate an ideal value for energy input by using the enthalpy of combustion of methane, $\text{CH}_4(\text{g})$:



The Efficiency of Natural Gas

When natural gas is used directly to provide heat, its efficiency can be as high as 97% (the efficiency of a high-efficiency furnace). Thus, for every mole of natural gas burned, you get about 778 kJ of energy (0.97×802.5 kJ). If natural gas is used to produce electrical energy in a power plant, however, the efficiency is much lower—about 37%. Why? The heat from burning the natural gas is used to boil water. The kinetic energy of the resulting steam is transformed to mechanical energy for turning a turbine, which generates the electrical energy. Each step has an associated efficiency that is less than 100%. Thus, at each step, the overall efficiency of the fuel decreases. **Figure 5.29** shows the difference between the home furnace and the power plant.

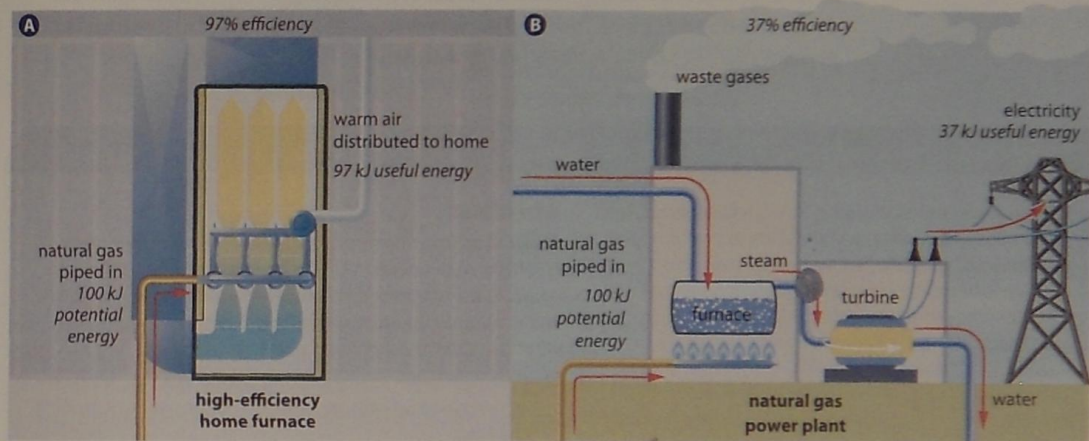


Figure 5.29 Natural gas is a far more efficient fuel when used to heat a home furnace than when it is used to generate electrical energy. There is only one energy conversion step in a high-efficiency furnace. Natural gas is burned, and the energy released heats air, which is distributed throughout the home (A). In a power plant, there are several energy conversions, and “waste” energy is released to the surroundings at each step (B).

The efficiencies of natural gas furnaces currently in use vary from 60% to 97%. The most energy-efficient gas furnaces on the market today are condensing furnaces. They, alone, can achieve efficiencies of 90% to 97% by using not only heat from the combustion of natural gas but also heat from the condensation of water vapour produced in the combustion process. When natural gas is burned, it produces a mixture of hot gases and water vapour. One of the main products of the combustion of natural gas is water vapour. The enthalpy of condensation of water is quite large, so when this water condenses, a large amount of energy is released. In older furnaces, the water vapour escaped out the exhaust. In the condensing furnace, a heat exchanger condenses the water vapour and the released heat adds to the heating of the house. The liquid water is released down a drain.

Energy Sources and the Environment

For many decades, people have become increasingly conscious of the effects of energy technologies on the environment. In evaluating the impact of energy sources on the environment, more and more people are asking themselves questions, such as:

- *Are any waste products or by-products of the energy production process harmful to living things or the environment?* Any process in which a hydrocarbon is burned produces carbon dioxide, a greenhouse gas. Greenhouse gases temporarily trap heat in Earth's atmosphere and delay the escape of heat into outer space. Many scientists have concluded that a build-up of greenhouse gases in the atmosphere is leading to an increase in global temperatures, known as global warming. In addition, any combustion process provides the heat required to form oxides of nitrogen from nitrogen gas. Oxides of nitrogen contribute to acid precipitation. Nuclear fission does not produce greenhouse gases, but it does leave behind radioactive waste that remains a danger for thousands of years.

- *Is obtaining or harnessing the fuel harmful to living things or the environment?* For example, strip coal mines and oil wells destroy habitats and harm living organisms. Although hydroelectric power plants produce very little in the way of emissions in the production of power, ecosystems both upstream and downstream of the plant are affected by their construction and presence.
- *Will using the energy source permanently remove the fuel from the environment?* A non-renewable energy source (such as coal, oil, or natural gas) is effectively gone once it is depleted. Non-renewable energy sources take millions of years to form and are used at a much faster rate than they can be replenished. A renewable energy source such as solar energy and wind energy can be replenished in a relatively short period of time. A somewhat renewable energy source is wood. Trees can be grown to replace those cut down. It takes trees a long time to grow, however, and habitats are often destroyed or permanently altered in the meantime by activities involved in logging.

Activity 5.3

Comparing Propane-driven and Gasoline-driven Cars

Vehicles that travel many kilometres on a regular basis, such as airline limousines and some taxis, often run on propane, $C_3H_8(g)$, instead of gasoline, because of its lower cost. In North America, however, vehicles are not manufactured to use propane—they must have their fuel systems converted to do so. What distance, in kilometres, must a vehicle be driven to recover the conversion cost?

Procedure

To begin to answer the above question, work in small groups to consider the following information. Also consider additional data that are needed to answer the question. Refer to Appendix B as necessary. Then use the points below to determine the distance needed to recover the conversion cost.

- Propane is a gas, but it is delivered to vehicles as a liquid under pressure. Gasoline is a mixture of hydrocarbons. For simplicity, assume that gasoline is pure octane, $C_8H_{18}(l)$.
- Automobiles are not manufactured to run on propane; they must be converted to be able to combust propane.
- Assume that both fuels, gasoline and propane, undergo complete combustion.
- Assume that the automobile travels a fixed distance per amount of energy, regardless of the fuel used to produce that energy.
- Assume the same efficiency of combustion for propane and gasoline.
- Assume that maintenance costs for a propane-powered car are the same as for a gasoline-powered car.

Questions

Note: You must calculate the distance, in kilometres, that a vehicle would need to be driven using propane, rather than octane (gasoline), to recover the cost of converting the vehicle to run on propane. You may solve the problem directly, or use the following points as a guide.

1. Calculate the enthalpy of combustion, ΔH_{comb} , for each of propane and octane. Express your answer in kJ/mol of the fuel.
2.
 - a. Using the gasoline (octane) consumption of the vehicle, calculate the energy required to travel 100 km.
 - b. Use your answer to part (a) to calculate the volume of liquid propane required for the vehicle to travel 100 km.
3.
 - a. Calculate the cost to travel 100 km using octane.
 - b. Calculate the cost to travel 100 km using propane.
 - c. Calculate the price difference between propane and octane, per 100 km travelled.
 - d. Use your answers to calculate the required distance, in kilometres, to travel before the fuel system conversion cost is recovered.
 - e. If an airport limousine travels an average of 200 km per day, how long would it take to recover the conversion cost?
4. Other than the fuel cost, what considerations could influence someone's decision to convert his or her vehicle to run on propane?
5.
 - a. What mass of $CO_2(g)$ is released into the atmosphere per 100 km of travel using octane?
 - b. What mass of $CO_2(g)$ is released into the atmosphere per 100 km of travel using propane?

Conventional Energy Sources in Ontario

Ontario has three main conventional sources of electrical energy: nuclear power plants, power plants that burn fossil fuels, and hydroelectric generating stations. The single largest source of electrical energy in Ontario in 2010 was nuclear power, as shown in **Figure 5.30**. Generating electrical energy using nuclear energy produces no greenhouse gases. However, uranium mining damages the environment, and radioactive nuclear waste products must be stored safely because they remain hazardous for thousands of years.

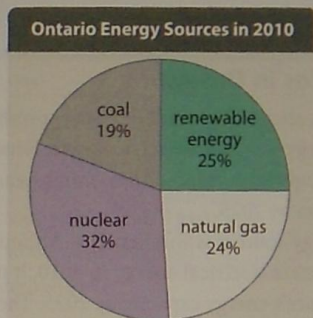


Figure 5.30 This graph shows the distribution of energy sources in Ontario in 2010. By 2025, renewable energy sources are projected to increase to 40 percent.

Analyze what percentage of Ontario's energy came from fossil fuels in 2010.

Another large source for generating electrical energy in Ontario is fossil fuels. Their main advantages are low costs, the large available supply of coal and natural gas, and the ability of power plants that burn fossil fuels to respond quickly to increased demand for electrical energy during hours of peak use. But the plants are only about 30% efficient, and the environmental costs are considerable, including carbon dioxide emissions. **Figure 5.31** summarizes issues associated with the use of fossil fuels.

Fossil Fuels and the Environment

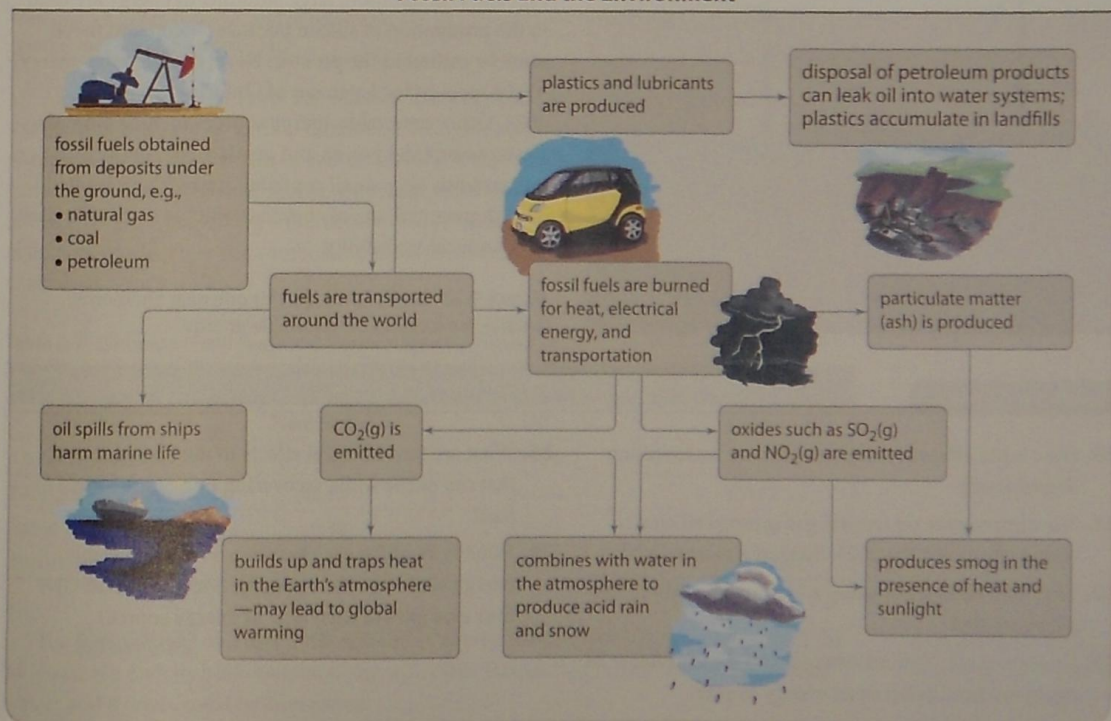


Figure 5.31 This concept map shows the interrelated issues that arise from the use of fossil fuels.

Hydroelectric Power: A Renewable Energy Resource

The third conventional source of energy comes from hydroelectric generating stations. Unlike nuclear power or fossil fuels, hydroelectric power is a renewable energy resource. Advantages of hydroelectric power are that there are no fuel costs, no combustion emissions, low operating costs, and it has high efficiency (about 90%). Disadvantages include the environmental effects of building dams, including the flooding of land and disruption of habitat. Once a dam is built, it does not use combustion of fossil fuels. However, the building of a dam is a tremendous task. The heavy equipment used during the construction of the dam uses large amounts of fossil fuels.

Alternative Renewable Energy Sources in Ontario

In 2010, renewable energy sources accounted for about 25 percent of energy production in Ontario. The major source of this renewable energy was hydroelectric power. Renewable energy sources are projected to become increasingly important in the coming years, perhaps reaching 40 percent of energy production by 2025.

One factor in the increase in renewable energy sources is wind energy. Although wind energy contributed only about 1 percent of Ontario's electrical energy in 2010, it might grow to provide 15 percent or more of the province's energy capacity by 2025. The cost of operating wind farms, such as the one shown in **Figure 5.32**, is very low, and they do not produce any chemical pollutants. The chief disadvantages are the great variation in winds at any site, the noise pollution produced, and the danger to birds that fly too near.

Solar energy is directly converted into electrical energy by solar cells. The primary advantage is that the energy is free and virtually unlimited in supply. However, solar energy has a low concentration at any particular location. Although the technology is improving, solar cells are not very efficient, and solar energy systems are expensive. In addition, large amounts of energy are used in the production of silicon because silicon and metal must be melted in the process. Nevertheless, solar energy might account for 5 percent of Ontario's energy by 2025. Other renewable energy sources include biomass, wave power, tidal power, and geothermal energy. All are currently very small contributors and have limited growth potential, mainly because of their costs or limited geographical availability.



Figure 5.32 Wind farms like this one near Shelburne, Ontario, are a source of renewable energy.

Learning Check

20. How is the efficiency of thermal energy conversion determined?
21. The dependency on natural gas is not predicted to change from 2010 to 2025. Suggest a reason for this.
22. List disadvantages of using a hydrocarbon source as a heating fuel.
23. Briefly compare the advantages and disadvantages of using nuclear fission as an energy source.
24. What are four harmful effects to the environment that can occur while recovering or using a source of fuel?
25. What is the difference between a non-renewable energy source and a renewable energy source? Give four examples of each type of energy source.

What Is a “Clean” Fuel?

Not all fossil fuels have the same impact on the environment, either during their recovery or in their use. Some fossil fuels are considered cleaner than others, meaning that their emissions are lower than those of others for an equivalent amount of energy produced.

Table 5.6 summarizes the carbon dioxide emissions for a variety of fuels in kilograms of $\text{CO}_2(\text{g})$ per kilojoule of energy produced.

Table 5.6 Fuel Source and Carbon Dioxide Emissions

| Fuel | Carbon Dioxide Emissions (kg/kJ of energy produced) |
|---|--|
| Anthracite coal | 108.83 |
| Lignite coal | 103.08 |
| Subbituminous coal | 101.79 |
| Bituminous coal | 98.25 |
| Municipal solid waste (landfill gas) | 95.64 |
| Wood and wood waste (biomass) | 93.32 |
| Tires/tire-derived fuel | 90.71 |
| Oil | 78.48 |
| Kerosene | 76.35 |
| Gasoline | 74.86 |
| Jet fuel | 74.78 |
| Propane | 66.61 |
| Flare gas | 57.77 |
| Natural gas (pipeline) | 56.03 |
| Methane | 55.16 |
| Nuclear | 0.00 |
| Renewables (solar, thermal, and photovoltaic; geothermal; wind; hydroelectric) | 0.00 |

As you can see from **Table 5.6**, renewable energy sources, such as wind power and solar power, produce no carbon dioxide in their operation. However, coal and natural gas produce a significant amount of carbon dioxide. Other emissions, such as particulates (ash particles) and oxides that combine with water to produce acid rain and snow, should also be factored in when evaluating a fuel source. From **Table 5.7**, it is clear that the levels of other pollutants produced in the combustion of three commonly used fossil fuels—coal, oil, and natural gas—vary widely.

Table 5.7 Common Fossil Fuels and Harmful Emission Levels

| Pollutant | Emission Levels (kg/MJ of energy produced) | | |
|--------------------|--|--------|---------|
| | Natural Gas | Oil | Coal |
| Carbon monoxide | 19.14 | 15.79 | 99.54 |
| Nitrogen monoxides | 44.03 | 214.40 | 218.70 |
| Sulfur dioxide | 0.48 | 536.95 | 1239.96 |
| Particulates | 3.35 | 40.20 | 1313.18 |

The **heat content** of a fuel is the amount of energy released per kilogram of the fuel. To fairly assess a fuel, its heat content, along with other factors that include its environmental impact and its cost, must be considered.

heat content of a fuel, is the amount of energy released per kilogram of the fuel

CHEMISTRY Connections

Deep Water Cooling

New technologies are using deep water cooling as an alternative to conventional air conditioning systems in office towers, thus significantly reducing energy use and its environmental impact. Deep water cooling takes advantage of the fact that at standard atmospheric pressure, water is most dense at 3.98°C , which causes it to sink. The bottom of any deep body of water is therefore at a constantly chilly temperature of 3.98°C , even during the hottest summers. Deep water cooling applies the second law of thermodynamics, which states that when two objects are in thermal contact, heat is always transferred from the object at a higher temperature to the object at a lower temperature until the two objects are at the same temperature.

The system works by pumping chilly water from the bottom of a lake into a heat transfer station. At the transfer station, the intake pipes come into thermal contact with a separate closed system of pipes containing a liquid—often water. Because the water in the closed system is warmer than the water in the intake pipes, thermal energy from the warmer water transfers to the cold lake water. The closed system of pipes—along with its now substantially colder water—leads into commercial buildings. Within the buildings' heat transfer systems, thermal energy from the surroundings is transferred to the cold water in the pipes, thereby cooling the buildings.

THE WORLD'S LARGEST DEEP WATER COOLING

SYSTEM Toronto-based Enwave Energy Corporation launched its deep water cooling system within the downtown Toronto-Dominion Centre in August 2004. The city is ideally situated to take advantage of Lake Ontario's cold deep-bottom water because the lake bed drops quickly and deeply within a few kilometres off shore. Enwave's three intake pipes draw water from 5 km off the shore of the lake at a depth of 83 m below the surface.

The cold deep-lake water is piped to the city's John Street Pumping Station, where it comes into thermal contact with Enwave's separate closed system of water pipes. At the station, heat exchangers transfer heat from the separate closed system to the lake water, in an exothermic process during which heat leaves the water of the closed system.

The pipes containing the newly chilled water then run from the transfer station into more than 60 of Toronto's downtown office towers, including the Air Canada Centre, the Royal Bank Plaza, and City Hall. Thermal energy from the buildings is transferred to the water in Enwave's closed

pipes, cooling the buildings. The water inside Enwave's network of pipes then returns to the John Street Pumping Station to repeat the cycle. After it has absorbed thermal energy at the John Street Pumping Station, the now warmer lake water is piped to the city's filtration plants and is used as part of the municipal drinking water supply.

THE BENEFITS OF DEEP WATER COOLING Enwave estimates that deep water cooling has led to decreased emissions of the greenhouse gas carbon dioxide by 79 000 tonnes annually, which is the equivalent of taking 15 000 cars off the road. The system has reduced emissions of the pollutants nitrogen oxide and sulfur oxide, both by-products of coal-fired power plants. Additionally, because Toronto uses the deep-lake water for its drinking supply, deep water cooling avoids having to return the warmed water to Lake Ontario, where it could harm numerous species adapted to living in cold water.



Enwave Energy Corporation uses the cold water of Lake Ontario for its deep water cooling system. For Toronto buildings using this system, there is about an 80 percent reduction in summertime energy consumption, compared with conventional air conditioning.

Connect to Society

1. What ideal conditions are required for a deep water cooling system to operate at maximum efficiency?
2. Who developed the concept of deep water cooling? What other cities use it?

Section 5.4 Review

Section Summary

- The efficiency of a chemical, physical, or nuclear process can be expressed as

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

- Every energy-conversion step in a process reduces its efficiency.
- Energy-conversion processes that involve boiling water into steam and using the steam to turn a turbine have low efficiencies.

- Fossil fuels are non-renewable resources. The burning of fossil fuels contributes to global warming, acid rain, and pollution of the environment.
- Renewable energy resources include hydroelectric power, solar energy, and wind energy. The use of renewable energy resources in Ontario to generate electricity is projected to increase substantially by 2025.

Review Questions

- K/U** What factors make natural gas more efficient as a fuel for home heating compared with its use as a fuel for a power plant?
- A** Heating and transportation uses come to mind when thinking of our dependency on fossil fuels. In what other ways do fossil fuels impact our life?
- K/U** Summarize the issues related to the use of fossil fuels. Suggest ways that you could contribute to reducing the use of fossil fuels.
- T/I** Compare the use of a wood waste biomass fuel with natural gas. Which fuel emits more $\text{CO}_2(\text{g})$ per kJ energy produced? Express as a percent.
- A** The cost of a propane barbecue is 90% of the cost of a natural gas barbecue. A hibachi, which burns charcoal, costs only 10% the cost of the gas barbecue. From an environmental and economic perspective, which type of barbecue would you choose? Justify your answer.
- A** A car has a calculated fuel consumption of 10.0 L/100 km (city) and 7.1 L/100 km (highway) according to the EnerGuide information. Overall, the actual fuel consumption has averaged 10.5 L/100 km.
 - Is this better or worse than the calculated fuel consumption?
 - Provide three reasons why the actual fuel consumption may be different from the calculated consumption.
 - List three ways in which the fuel consumption could be improved.
- A** You have probably noticed that a lot of heat is generated by the compressor of your refrigerator. Design a system that could apply this and other sources of "waste heat" in your home for some useful purpose.
- A** You are about to purchase a new washing machine. As an energy-conscious consumer, what information would you look for to assess its efficiency?
- C** What is meant by a "clean" fuel? Are there really any clean fuels? Justify your answer in a brief, well-reasoned paragraph.
- K/U** Identify the products of combustion associated with the following environmental issues:
 - global warming
 - acid rain or snow
 - smog
- K/U** Differentiate between the *heat content* and *enthalpy of combustion* of a fuel. Which term is more useful in evaluating fuels? Why?
- T/I** The complete combustion of 1.00 mL of octane increases the temperature of 250.00 g of water by 22.7°C. The density of octane is 0.70 g/mL. What is the efficiency of the octane in heating the water?
- T/I** Based on the data below, is octane or ethanol a better fuel per unit volume?

For octane:
density = 0.70 g/mL; $\Delta H_{\text{comb}}^\circ = -44.5 \text{ kJ/g}$
efficiency of heat to mechanical energy = 20.0%

For ethanol:
density = 0.79 g/mL; $\Delta H_{\text{comb}}^\circ = -29.7 \text{ kJ/g}$
efficiency of heat to mechanical energy = 25.0%
- T/I** The complete combustion of methane is represented in the following equation:
$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 802.5 \text{ kJ}$$

Assume that natural gas is essentially methane. The emission level of carbon monoxide, $\text{CO}(\text{g})$, from the burning of natural gas is 19.14 kg/MJ of energy produced. What mass of $\text{CO}(\text{g})$ will be emitted when 100.0 g of natural gas is burned?

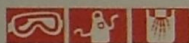
Plan Your Own INVESTIGATION

5-A

Skill Check

- ✓ Initiating and Planning
- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Safety Precautions



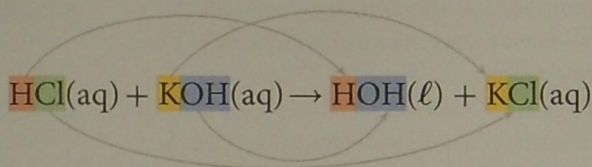
- If you get any hydrochloric acid or sodium hydroxide solution on your skin, immediately flush with plenty of cold water.
- Wear safety eyewear throughout this investigation.
- Wear a lab coat or apron throughout this investigation.

Suggested Materials

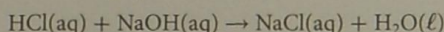
- 1.00 mol/L HCl(aq) at room temperature
- 1.00 mol/L NaOH(aq) at room temperature
- simple calorimeter (two nested polystyrene cups in a 250 mL beaker, with a two-holed polystyrene lid)
- 100 mL graduated cylinder
- thermometer (alcohol or digital)
- stirring rod

Determining the Enthalpy of a Neutralization Reaction

As you have learned, the reaction between an acid and a base is often called a neutralization reaction. In a neutralization reaction, the acid is considered to counteract (or neutralize) the properties of the base, and the base counteracts the properties of the acid. As shown below, for a neutralization reaction between an Arrhenius acid and an Arrhenius base, the hydrogen ions from the acid, $\text{H}^+(\text{aq})$, react with the hydroxide ions, $\text{OH}^-(\text{aq})$, of the base to produce water. The metal cation of the base and the anion from the acid combine to form a salt.



In this investigation, you will study the reaction between a hydrochloric acid solution and a sodium hydroxide solution. This neutralization reaction is represented by the following equation:



Using a simple calorimeter, you will determine the enthalpy change for this reaction.

Pre-Lab Questions

1. Explain the benefit of letting the solutions of HCl(aq) and NaOH(aq) sit overnight.
2. When using the same graduated cylinder to measure the volumes of HCl(aq) and NaOH(aq), it is important to rinse the cylinder with water and a small amount of the second reactant before measuring the volume of the second reactant. Explain why this is important for this investigation.
3. Describe how to perform each of the following safely:
 - diluting a strong acid solution with water
 - dissolving a solid base in water
 - adding a solution of base to a solution of acid
4. If acid comes in contact with your skin, why must you flush the area with plenty of cold water, rather than neutralizing the acid with a base?

Question

What is the enthalpy of neutralization for the reaction between solutions of HCl(aq) and NaOH(aq)?

Plan and Conduct

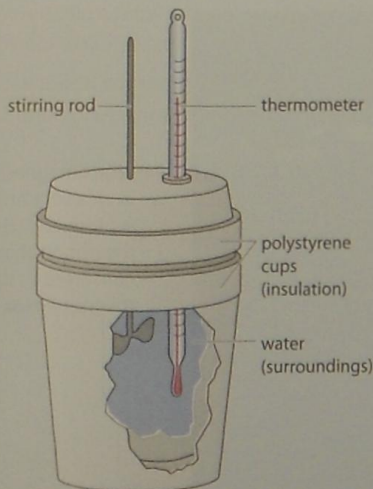
1. Write a complete and detailed procedure for performing this investigation. Make sure to include all safety precautions that must be followed.

Go to Organizing Data in a Table in Appendix A for information about designing data tables.

2. Prepare a table to record your observations. Decide at what time intervals you will record your observations.
3. Use **Figure 5.16**, which is also represented below for easy reference, to build a simple calorimeter. Be sure that the lid has two holes—one for the thermometer and one for the stirring rod. The holes should be as small as possible to minimize thermal energy exchange with the surroundings. Also, be sure to place the calorimeter within the 250 mL beaker to help secure it in an upright position.
4. Have your teacher approve your procedure, as well as the calorimeter you have assembled, before proceeding with the investigation.
5. If time permits, carry out a duplicate trial.
6. Dispose of any chemicals as instructed by your teacher.
7. Compare data from other classmates with your own data.

Analyze and Interpret

1. Calculate the quantity of thermal energy absorbed by the solution in the calorimeter and the quantity of thermal energy released by the reaction. State any assumptions you made in order to carry out your calculations.
2. Calculate the amount in moles of HCl(aq) and of NaOH(aq) involved in the reaction.
3. Use the answers to questions 1 and 2 to calculate the ΔH for the given neutralization reaction, in units of kilojoules per mole of the limiting reagent. (If HCl(aq) and NaOH(aq) are present in equimolar amounts, either one can be considered to be the limiting reagent.)
4. Is the neutralization reaction exothermic or endothermic? What is the sign—positive or negative—of ΔH ?



Conclude and Communicate

5. Write the thermochemical equation for the neutralization reaction.
6. Compare the enthalpy of neutralization that you determined with those of your classmates.
7. Your teacher will provide you with the enthalpy of neutralization value that is reported in the literature. How does this value compare with your experimentally determined value?
8. Discuss possible sources of error for this investigation, which could have contributed to the discrepancies between values determined within your class and between your value and the reported value.

Extend Further

9. **INQUIRY** Write the thermochemical equation for the neutralization of HCl(aq) using solid sodium hydroxide, NaOH(s) , instead of NaOH(aq) . Would you expect the ΔH value to differ from that obtained using NaOH(aq) ? Explain briefly.
10. Design an investigation to determine if using solid NaOH instead of NaOH(aq) will have any effect on the ΔH value for the neutralization reaction. If your teacher approves your procedure, carry out the investigation.
11. Design an experiment to determine if the acid involved in a neutralization investigation has any effect on the ΔH of the reaction. If your teacher approves your procedure, carry out the investigation.
12. **RESEARCH** On August 5, 2005 a CN train derailment north of Squamish, British Columbia, released about 40 000 L of a 73% (m/v) solution of sodium hydroxide into the Cheakamus River. Use Internet resources to determine the immediate effects of this spill on the local ecosystem. How was the spill eventually cleaned up? How did officials know that their clean-up efforts were successful?

This simple calorimeter can be used to measure the enthalpy change for the neutralization reaction between HCl(aq) and NaOH(aq)

Skill Check

Initiating and Planning

- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Safety Precautions



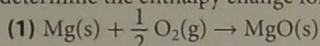
- Hydrochloric acid is corrosive. Use care when handling it. Hydrochloric acid fumes also cause burning to the linings of the nose and throat when inhaled.
- Be careful not to inhale the magnesium oxide powder.

Materials

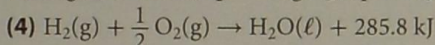
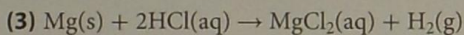
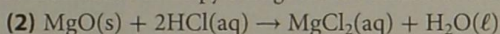
- 1.00 mol/L HCl(aq)
- MgO(s) powder
- Mg ribbon (or Mg turnings)
- simple calorimeter
- 100 mL graduated cylinder
- scoop
- electronic balance
- thermometer (alcohol or digital)
- sandpaper or emery paper

Hess's Law and the Enthalpy of Combustion of Magnesium

Magnesium ribbon burns in air in a highly exothermic combustion reaction. (See equation (1) below.) A very bright flame accompanies the production of magnesium oxide. It is impractical and dangerous to use a simple calorimeter to determine the enthalpy change for this reaction:



Instead, you will determine the enthalpy changes for two other reactions (equations (2) and (3) below). You will use these enthalpy changes, along with the known enthalpy change for another reaction (equation (4) below), to determine the enthalpy change for the combustion of magnesium.



Notice that reactions represented in equations (2) and (3) occur in aqueous solution. You can use a simple calorimeter to determine the enthalpy changes for these reactions. Equation (4) represents the formation of water directly from its elements in their standard state.

Pre-Lab Questions

- Explain how Hess's law allows you to determine the enthalpy of a reaction without carrying out the reaction.
- What type of data do you need in order to use Hess's law?
- Describe the safety precautions you must follow when working with a strong acid.

Question

What is the molar enthalpy of combustion of magnesium?



When magnesium ribbon burns in air a very bright white flame is produced. The lower part of the ribbon shown here has been converted to the solid, white magnesium oxide product.

Procedure

Part 1: Determining ΔH of Reaction (2)

1. Read the Procedure for Part 1. Prepare a data table to record mass and temperature data.
2. Set up the simple calorimeter. Using a graduated cylinder, add 100 mL of 1.00 mol/L HCl(aq) to the calorimeter.
3. Record the initial temperature, T_{initial} , of the HCl(aq), to the nearest tenth of a degree.
4. Find the mass of no more than 0.80 g of MgO(s) powder. Record the exact mass.
5. Add the MgO(s) powder to the calorimeter containing the HCl(aq). Swirl the solution gently, recording the highest temperature, T_{final} , reached.
6. Dispose of the reaction solution as directed by your teacher.

Part 2: Determining ΔH of Reaction (3)

1. Read the Procedure for Part 2. Prepare a data table to record mass and temperature data.
2. Using a graduated cylinder, add 100 mL of 1.00 mol/L HCl(aq) to the calorimeter.
3. Record the initial temperature, T_{initial} , of the HCl(aq) to the nearest tenth of a degree.
4. If you are using magnesium ribbon (as opposed to turnings), sand the ribbon. Accurately determine the mass of no more than 0.50 g of magnesium. Record the exact mass.
5. Add the Mg(s) to the calorimeter containing the HCl(aq). Swirl the solution gently, recording the highest temperature, T_{final} , reached.
6. Dispose of the solution as directed by your teacher.

Analyze And Interpret

1. Determine the enthalpy of reactions for reactions (2) and (3). List any assumptions you make and explain why they are valid assumptions.
2. Write thermochemical equations for reactions (2) and (3) using ΔH notation. Ensure the signs you use are correct.

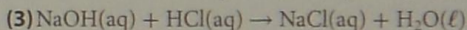
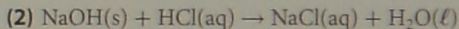
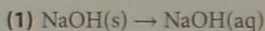
3. Algebraically combine equations (2), (3), and (4), and their corresponding ΔH values, to arrive at equation (1) and the molar enthalpy of combustion of magnesium.
4. Draw an enthalpy diagram to represent the combining of equations (2), (3), and (4) to obtain equation (1) and the molar enthalpy of combustion of magnesium.
5. Compare your result with the accepted value of ΔH_{comb} for magnesium. Calculate your percent error.
6. Suggest some sources of error in the procedure. In what ways could you improve the procedure?

Conclude and Communicate

7. Explain how you used Hess's law to determine ΔH for the combustion of magnesium. State the result you obtained for the thermochemical equation that corresponds to chemical equation (1).

Extend Further

8. **INQUIRY** Design an investigation to test Hess's law by using the following equations:



Assume you have a simple calorimeter, NaOH(s), 1.00 mol/L HCl(aq), 1.00 mol/L NaOH(aq), and standard laboratory equipment. Write a step-by-step procedure for the investigation. Then outline a plan for analyzing your data. Be sure to include appropriate safety precautions. If time permits, obtain your teacher's approval and carry out the investigation.

9. **RESEARCH** Burning magnesium not only creates a very bright light but it also burns at a very high temperature. Research ways in which people have used the bright light and high temperatures in the past and currently.

Case Study

Comparing Ethanol and Biodiesel

Is One Option Greener?

Scenario

You are an energy analyst for Natural Resources Canada. You have been asked to ensure that various federal government policies result in the greatest benefits for the environment. The government is seeking to reduce greenhouse gas emissions by boosting the production and use of biofuels. Biofuels are fuels made from plant and animal materials. Some examples of biofuels include ethanol, which can be made from corn or wheat, and biodiesel, which can be made from tallow (animal fat) or canola.

Replacing Fossil Fuels

Each biofuel burns in an engine in a way that is similar to the combustion of a certain kind of fossil fuel. Ethanol has a boiling point similar to that of gasoline. Thus, it can be mixed with gasoline and then burned in a regular car engine. Diesel has a higher boiling point than gasoline, so diesel engines use a different method to ignite fuel compared with gasoline engines. Biodiesel has a boiling point similar to that of diesel. Therefore, it can replace diesel in a diesel engine.

Unlike fossil fuels, biofuels are renewable. They will not run out because they can be replenished when farmers grow more plants or raise more animals. Additionally, plants and animals take in carbon from the environment as they grow, thereby compensating for the carbon dioxide that is released into the atmosphere when biofuels are burned. This balancing of carbon absorption and emission means that biofuels have no net effect on the amount of carbon in the atmosphere. Biofuels are therefore sometimes described as “carbon neutral.”

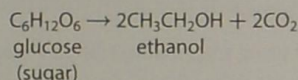
However, that description does not take into account the extra energy inputs required to produce and distribute biofuels. These energy inputs include the fuel consumed by farm machinery and by the trucks that deliver ethanol to gas stations. Other energy inputs involved in the manufacture of ethanol and biodiesel include the energy in the chemical reactions used to convert raw corn and canola into ethanol and biodiesel.

The steps in the manufacturing process are all part of the life cycle of a biofuel. Scientists use computer models called “life-cycle assessments” to add up the values for all the energy inputs involved in producing a particular fuel. They then compare the total energy input with the

energy output—the amount of energy released when the fuel is burned. They can do similar calculations involving greenhouse gas inputs and outputs. By comparing the life cycles of two fuels, such as ethanol and gasoline, scientists can determine the extent to which greenhouse gas emissions will change if one fuel replaces another.

How Are Ethanol and Biodiesel Manufactured?

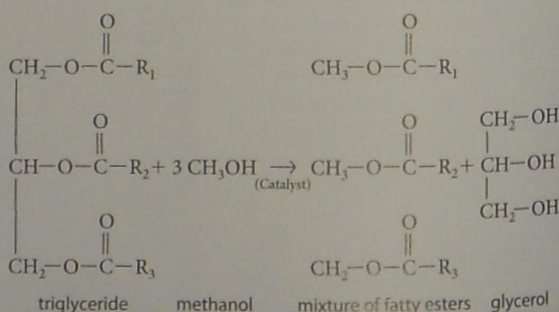
In Canada, ethanol begins its life cycle as either corn or wheat (Canada’s most plentiful crop). The corn or wheat is harvested and transported by truck or by train to a factory. There, sugars in the grains are fermented (converted into liquid alcohol) by the action of yeast according to the following chemical reaction:



The ethanol is distilled off, and the solid material left behind is used for animal feed.

Biodiesel is made of molecules called fatty esters. In a factory, a chemical reaction called transesterification can convert almost any plant and animal fats and oils into fatty esters (and therefore biodiesel). The chemical process that results in this conversion involves mixing plant and animal fats made of molecules called triglycerides with methanol (a type of alcohol) in the presence of a catalyst.

Each triglyceride contains three chains of carbon and hydrogen atoms (called fatty acid chains and labelled R_1 , R_2 , and R_3 as shown in the equation below). The transesterification reaction breaks each triglyceride into three fatty esters (one for each fatty acid chain) and one molecule of glycerol, a type of alcohol used in many foods, cosmetics, and drugs.



Since 2010, a law has stipulated that all gasoline in Canada must contain 5 percent ethanol. Starting in 2011, all heating oil must contain 2 percent biodiesel. Currently, the Canadian federal government is trying to decide how and where to target new rules and incentives to boost the production of biofuels. In your role as energy analyst, you must assess whether ethanol is greener than biodiesel or vice versa. You need to compare the energy required to produce these biofuels, as well as the greenhouse gases that these biofuels release during their life cycle, against the fossil fuels they replace.

Hi Sarah,

As requested, here are the data from our life-cycle assessments of different fuels to help you with your analysis of their environmental impacts.

| Comparison of Energy Input and Energy Output of Selected Fuels | | | | |
|--|-------|---------|--------|-----------|
| | Gas | Ethanol | Diesel | Biodiesel |
| Energy input (MJ/L) | 9.96 | 16.16 | 9.85 | 8.33 |
| Energy output (MJ/L) | 34.69 | 23.58 | 38.65 | 36.9 |

The energy output of each fuel is the amount of energy released when 1 L of the fuel is burned. The energy input of each fuel is the amount of energy consumed to produce 1 L of the fuel.

Sincerely,

Carlo Singh

Renewable Fuels Research Group

Research and Analyze

1. Conduct research to determine the steps that are involved in the life cycle of ethanol and biodiesel, from planting the crop to burning the fuel in your car engine or home. What energy inputs are required? Which steps in each life cycle consume energy and which steps release energy? Which steps consume or release greenhouse gases?
2. Conduct research to determine the steps that are involved in the life cycle of gasoline and diesel. Which steps in their life cycle are similar to those of biofuels? Which steps are different?
3. Analyze the energy efficiencies of diesel, biodiesel, gasoline, and ethanol by answering the following questions. Use the data in the email at left.
 - a. The net energy ratio describes the energy output (in joules) for each joule of energy input involved in making and distributing a fuel. This ratio can be a measure of efficiency. Use this equation to calculate the net energy ratio for each fuel:

$$\text{net energy ratio} = \frac{\text{output}}{\text{input}}$$

- b. Calculate the energy input (in megajoules) to produce 7 L of gasoline—enough to fuel a Toyota Matrix for 100 km. (Hint: What is the energy input (in megajoules) to produce 1 L of gas?). Assume that the car always requires the same energy output to travel the same distance, no matter what fuel it is using. Determine the energy input (in megajoules) to produce enough diesel, biodiesel, or ethanol to fuel the car for 100 km.

Take Action

1. **PLAN** In a group, discuss how diesel compares with biodiesel and how ethanol compares with gasoline in terms of efficiency. How do biodiesel and ethanol compare with each other in terms of efficiency? Think about the processes involved in producing these fuels. Suggest some ways to use other “side products” such as heat. Describe energy inputs that could be changed to make the process more energy efficient.
2. **ACT** Write a report to your supervisor explaining whether you think replacing gasoline with ethanol made from corn or replacing diesel with biodiesel made from canola would have a more positive impact on the environment.

Chapter 5 SUMMARY

Section 5.1 The Nature of Energy and Heat

All chemical reactions and nuclear reactions, and many physical processes, are accompanied by changes in energy that can be measured.

Key Terms

| | |
|--|------------------------------|
| closed system | isolated system |
| endothermic | open system |
| enthalpy, H | second law of thermodynamics |
| enthalpy of solution, $\Delta H_{\text{solution}}$ | specific heat capacity, c |
| exothermic | temperature |
| first law of thermodynamics | thermal energy |
| | thermochemistry |

Key Concepts

- A system is the object or substance being studied, and the surroundings are everything else in the universe. Systems can be open, closed, or isolated.
- Open and closed systems can exchange energy with the surroundings by exchanging heat with the surroundings,

by doing work on the surroundings, or by the surroundings doing work on the system.

- The first law of thermodynamics states that energy cannot be created or destroyed but can be transformed from one type of energy to another type of energy or transferred from one object to another object.
- The second law of thermodynamics states that, when two objects are in thermal contact, heat will be transferred from the object at a higher temperature to the object at the lower temperature until they reach thermal equilibrium.
- An enthalpy change in a system, occurring at constant pressure, is the same as the amount of heat that is exchanged between the system and its surroundings. Enthalpy changes can be positive or negative and depend only on the initial and final states of the system.
- The range of enthalpy changes is lowest for physical changes, intermediate for chemical changes, and highest for nuclear changes.

Section 5.2 Thermochemical Equations and Calorimetry

When a process such as a chemical reaction takes place at constant pressure, the enthalpy change of the process is equal to the amount of heat exchanged between the system and its surroundings.

Key Terms

| | |
|------------------|--------------------|
| bomb calorimeter | calorimetry |
| calorimeter | simple calorimeter |

Key Concepts

- When a process takes place under conditions of constant pressure, the enthalpy change of a system is equal to the amount of heat gained or heat lost by the system.
- The standard enthalpy of a reaction as written (ΔH_r°) is the enthalpy change for the amount in moles of each reactant and product as determined by the coefficient of the term in the chemical equation.

- A process taking place in a simple calorimeter occurs at constant pressure. Therefore, the amount of heat that is exchanged between the calorimeter and the system is equal to the change in the enthalpy of the system.
- Temperature data from a simple calorimetry experiment can be used to calculate the enthalpy of a chemical reaction.
- The standard enthalpy of combustion ($\Delta H_{\text{comb}}^\circ$) of a compound is the enthalpy change that occurs when 1 mol of a compound reacts completely with oxygen under the conditions that the reactants started out at 25°C and 100 kPa of pressure and the products cooled to 25°C and 100 kPa of pressure after the reaction was complete.
- A process taking place in a bomb calorimeter occurs at constant volume but not constant pressure.

Section 5.3 Hess's Law

According to Hess's law, if a series of chemical equations are added together, then the enthalpy of reaction for the final equation is the sum of the enthalpy changes for the series of equations.

Key Terms

| | |
|--|-------------------|
| Hess's law | thermal stability |
| standard molar enthalpy of formation, ΔH_f° | |

Key Concepts

- Hess's law states that the enthalpy change of a physical or chemical process depends only on the initial and final conditions. The enthalpy change of the overall process is the sum of the enthalpy changes of its individual steps.
- You can add any number of chemical equations to obtain an equation that you need, and the enthalpy change of the overall reaction is the sum of the enthalpy changes of the individual reactions.

- You can manipulate chemical equations to make them fit into another set of reactions by multiplying the equations by a constant or by reversing the equations. If you multiply by a constant, you must multiply the enthalpy change by that same constant. If you reverse an equation, you must change the sign of the enthalpy change.
- The standard enthalpy of formation of a compound, ΔH_f° , is the enthalpy change for the formation of 1 mol of the compound from its elements in their most stable state under standard conditions.
- The enthalpy of formation of an element in its most stable state under standard conditions is arbitrarily set at zero.
- You can calculate the enthalpy change for any reaction by applying the formula

$$\Delta H_r^\circ = \sum (n\Delta H_f^\circ \text{ products}) - \sum (n\Delta H_f^\circ \text{ reactants})$$

Section 5.4

Energy Efficiency and Energy Resources

Energy sources are not and cannot be 100% efficient, and energy sources vary greatly in their environmental, societal, and economic impacts.

Key Terms

efficiency

heat content

Key Concepts

- The efficiency of a chemical, physical, or nuclear process can be expressed as

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

- Every energy-conversion step in a process reduces its efficiency.

- Energy-conversion processes that involve boiling water into steam and using the steam to turn a turbine have low efficiencies.
- Fossil fuels are non-renewable resources. The burning of fossil fuels contributes to global warming, acid rain, and pollution of the environment.
- Renewable energy resources include hydroelectric power, solar energy, and wind energy. The use of renewable energy resources in Ontario to generate electricity is projected to increase substantially by 2025.

Knowledge and Understanding

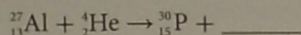
Select the letter of the best answer below.

- Hot soup is kept in a closed, insulated bottle at 60.0°C . The bottle is left near a heat source where the surrounding temperature is 35.0°C . Select the statement that correctly describes the bottle and its contents after 2 h.
 - closed system, temperature greater than 60.0°C
 - isolated system, temperature at 60.0°C
 - open system, temperature less than 60.0°C
 - closed system, temperature less than 60.0°C
 - isolated system, temperature less than 60.0°C
- Select the correct statement from the following:
 - Thermal energy is the sum of the potential energies of all the particles in a sample.
 - For an isolated system we can say:
universe = system
 - The particles in two samples of the same material at the same temperature have the same average kinetic energy.
 - Melting an ice cube by holding it in your bare hand results in a decrease in the kinetic energy of particles of $\text{H}_2\text{O}(\text{s})$.
 - The use of a wood stove to heat a room is an example of a closed system.
- The standard molar enthalpy of formation of a compound represents
 - the thermal energy released when 1 mol of a compound decomposes.
 - the enthalpy change when 1 mol of a compound is formed from its element at standard conditions.
 - the enthalpy change when 1 mol of an element changes to a compound.
 - the heat energy released when 1 mol of a compound undergoes complete combustion.
 - the enthalpy change when 1 mol of a compound undergoes a phase change.

4. Which of the following represents the enthalpy of solution?

a. $\Delta H_{\text{solvent}} + \Delta H_{\text{solute}}$
 b. $\Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$
 c. $\Delta H_{\text{solvent}} + \Delta H_{\text{solute}} + \Delta H_{\text{mix}}$
 d. $\Delta H_{\text{solvent}} + \Delta H_{\text{solution}}$
 e. none of the above

5. What is the missing particle in the nuclear reaction written below?

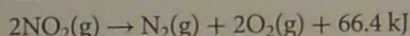


a. ${}^1_1\text{H}$
 b. ${}^0_{-1}\text{e}$
 c. ${}^1_0\text{n}$
 d. ${}^0_{+1}\text{e}$
 e. ${}^1_1\text{P}$

6. You have a sample of oxygen gas at SATP. To increase the total thermal energy you could

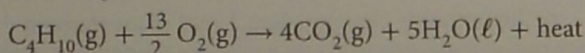
a. decrease the temperature of the sample at constant pressure.
 b. increase the pressure on the sample at constant temperature.
 c. insulate the sample from the surroundings.
 d. change the specific heat capacity of the sample to a higher value.
 e. increase the mass of the sample.

7. Which combination of statements is correct for the reaction below?



a. exothermic, potential energy greater in reactants
 b. exothermic, potential energy greater in products
 c. endothermic, potential energy greater in products
 d. endothermic, potential energy less in reactants
 e. endothermic, potential energy less in products

8. Identify the correct expression that can be used to determine the change in thermal energy for the following reaction:



a. $\Delta H_r^\circ = \left[(4 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (5 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell)) \right] + \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g})) + \left(\frac{13}{2} \text{ mol} \right)(\Delta H_f^\circ \text{O}_2(\text{g})) \right]$
 b. $\Delta H_r^\circ = \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g})) + \left(\frac{13}{2} \text{ mol} \right)(\Delta H_f^\circ \text{O}_2(\text{g})) \right] - \left[(4 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (5 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell)) \right]$

c. $\Delta H_r^\circ = \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g})) + \left(\frac{13}{2} \text{ mol} \right)(\Delta H_f^\circ \text{O}_2(\text{g})) \right] + \left[(4 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (5 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell)) \right]$

d. $\Delta H_r^\circ = \left[(4 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + (5 \text{ mol})(\Delta H_f^\circ \text{H}_2\text{O}(\ell)) \right] - \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g})) + \left(\frac{13}{2} \text{ mol} \right)(\Delta H_f^\circ \text{O}_2(\text{g})) \right]$

e. $\Delta H_r^\circ = \left[(1 \text{ mol})(\Delta H_f^\circ \text{CO}_2(\text{g})) + \left(\frac{4}{5} \text{ mol} \right)(\Delta H_f^\circ \text{H}_2\text{O}(\ell)) \right] - \left[(1 \text{ mol})(\Delta H_f^\circ \text{C}_4\text{H}_{10}(\text{g})) + \left(\frac{13}{2} \text{ mol} \right)(\Delta H_f^\circ \text{O}_2(\text{g})) \right]$

9. Electrical energy used to heat a building can be generated by the following sequence of steps:

(1) Kinetic energy of water flowing in a river turns turbines to generate electricity.
 (2) Electrical energy is sent through transmission lines.
 (3) Electrical energy is used to operate a heating unit.

Which statement about this energy flow is correct?

a. The first law of thermodynamics holds for steps (1) and (2) but not for step (3).
 b. The overall efficiency is less than 100% because energy is lost to the surroundings in each step.
 c. The second law of thermodynamics holds only for step (3).
 d. The potential energy of the system increases in step (1) and decreases in steps (2) and (3).
 e. The potential energy of the system increases in steps (2) and (3).

10. Which equation correctly represents the standard molar enthalpy of formation, ΔH_f° , for aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3(\text{s})$?

a. $\text{Al}_2(\text{SO}_4)_3(\text{s}) \rightarrow 2\text{Al}(\text{s}) + \frac{3}{8}\text{S}_8(\text{s}) + 12\text{O}(\text{g})$
 b. $2\text{Al}(\text{s}) + \frac{1}{8}\text{S}_8(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{s})$
 c. $\text{Al}_2(\text{SO}_4)_3(\text{s}) \rightarrow 2\text{Al}(\text{s}) + 3\text{S}(\text{s}) + 12\text{O}_2(\text{g})$
 d. $2\text{Al}(\text{s}) + \frac{3}{8}\text{S}_8(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{s})$
 e. $\text{Al}(\text{s}) + \frac{1}{8}\text{S}_8(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{s})$

11. The development of which one of the following energy sources has the *least* negative impact on the environment?

a. solar
 b. coal
 c. biomass
 d. natural gas
 e. hydroelectricity

12. You are using a bomb calorimeter that is calibrated at $7.8 \text{ kJ/}^\circ\text{C}$ to measure the energy content of food in kJ/g . Select the piece of information *not* required to complete the calculation for energy content.

- initial temperature
- heat capacity of the calorimeter
- mass of water in the calorimeter
- mass of food
- final temperature

13. When two compounds are compared, the one having the more negative value for its enthalpy of formation will be the more thermally stable. This is true because

- bonds are broken in decomposition but are made during formation.
- formation reactions use elements and decomposition involves compounds.
- formation is the reverse of decomposition; more energy given off during formation means more energy to be added for decomposition.
- formation reactions are exothermic and decomposition reactions are endothermic.
- compounds have more potential energy compared with their elements.

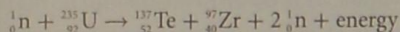
14. A condensing furnace fuelled by natural gas is more efficient than a conventional furnace using the same fuel because

- a condensing furnace allows for comparatively more complete combustion of natural gas.
- the ideal mixture of air and natural gas can be adjusted.
- carbon dioxide gas can be compressed into a liquid.
- energy is recovered from the water vapour.
- water vapour is allowed to escape.

Answer the questions below.

15. What is the meaning of the term *energy*? State the law of conservation of energy.

16. You are given the following equation:



- Classify the reaction represented by this equation.
- What is the source of the energy released in this reaction?

17. Water at 90.0°C is heated to 110.0°C at standard pressure. Describe the energy conversions that occur and what is happening at the molecular level during these changes.

18. A wax candle is lit and is allowed to burn until the air temperature in the room increases by 0.50°C .



- Use this example to explain the difference between the terms *system* and *surroundings*.
 - Express the first law of thermodynamics in words and by means of a mathematical equation.
19. One reaction occurs at constant pressure and another reaction occurs at constant volume. What does the amount of heat exchanged between the system and its surroundings represent for these two reactions?
20. On which two laws of thermodynamics is calorimetry based? Briefly outline how each of these laws makes calorimetric calculations possible.
21. For calculations using a bomb calorimeter, why is the heat capacity of the calorimeter used rather than the specific heat capacity?
22. Consider the reaction $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) + 11 \text{ kJ} \rightarrow \text{N}_2\text{O}_4(\text{g})$.
- Which has more potential energy: the reactants or the product?
 - Explain what this means in terms of the bonding in the reactant and product molecules.
23. An investigation to determine the heat content of an alcohol is carried out. The heat released is collected in an aluminum can that is holding water, which is acting as a flame calorimeter. After the investigation, black soot on the bottom of the calorimeter can be seen.
- What does this black soot indicate?
 - How will this affect the accuracy of your calculations?
 - What information must be recorded to determine the heat content of the alcohol?
24. For an exothermic reaction, are there more and/or stronger bonds in the reactants or in the products? Explain using the complete combustion of methane as an example.

25. List five activities in your daily life that depend on the use of fossil fuels. Name the fuel.
26. When using the expression for the calculation of efficiency, give examples of what could be included as input energy and output energy.
27. A crop such as corn can be used to produce ethanol. Ethanol is a fuel with an enthalpy of combustion of 278 kJ/mol. Is ethanol produced in this way a renewable resource? Give reasons for your answer.
28. When ammonium chloride, $\text{NH}_4\text{Cl}(\text{s})$, is dissolved in water, moisture is observed to condense on the side of the beaker, and a short time later, ice has formed that freezes the beaker to the table top. Briefly explain what has happened.

Thinking and Investigation

29. Define each word in the term *standard molar enthalpy of formation*. Use the equation as written below to determine the standard molar enthalpy of formation for $\text{Cr}_2\text{O}_3(\text{s})$.
- $$2\text{Cr}_2\text{O}_3(\text{s}) + 2256.84 \text{ kJ} \rightarrow 4\text{Cr}(\text{s}) + 3\text{O}_2(\text{g})$$
30. Use the information listed below to determine ΔH° for the reaction as written:
- $$\text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\ell)$$
- (1) $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\ell) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$ $\Delta H^\circ = -65.2 \text{ kJ}$
 (2) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\Delta H^\circ = +178.1 \text{ kJ}$
 (3) $\text{Ca}(\text{OH})_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$ $\Delta H^\circ = -16.2 \text{ kJ}$
31. Equal masses of water and an unknown liquid are heated by the same heat source for the same period of time. The temperature of the unknown liquid increases twice as much as the temperature of the water. What conclusion can be drawn from this information?
32. The molar enthalpy of formation for copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2(\text{s})$, is -302.9 kJ/mol .
- a. Write the thermochemical equation for the decomposition of $\text{Cu}(\text{NO}_3)_2(\text{s})$ to its elements.
 b. Calculate the amount of thermal energy required to produce 37.9 g of copper metal.
33. Given the information
- $$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H_r^\circ = +57.2 \text{ kJ}$$
- is the following correct? Briefly explain your reasoning.
- $$\text{NO}_2(\text{g}) \rightarrow \frac{1}{2}\text{N}_2\text{O}_4(\text{g}) \quad \Delta H_r^\circ = -57.2 \text{ kJ}$$
34. A 62.16 g sample of molten lead solidifies, exchanging 98.1 kJ of energy with the surroundings.
- a. What is the enthalpy of melting, $\Delta H_{\text{melt}}^\circ$, for lead?
 b. Write the thermochemical equation for the solidification of $\text{Pb}(\ell)$.
35. A 10.0 g sample of phosphorus, $\text{P}_4(\text{s})$, is reacted with chlorine gas to form phosphorus(III) chloride, $\text{PCl}_3(\text{g})$. The enthalpy change for the reaction is -23.2 kJ . Write the equation for the standard molar enthalpy of formation, ΔH_f° , for $\text{PCl}_3(\text{g})$.
36. Use the given equations and Hess's law to determine the enthalpy of reaction when propyne, $\text{C}_3\text{H}_4(\text{g})$, reacts with hydrogen gas, $\text{H}_2(\text{g})$, to form propane, $\text{C}_3\text{H}_8(\text{g})$.
- (1) $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H^\circ = +285.8 \text{ kJ}$
 (2) $\text{C}_3\text{H}_4(\text{g}) + 4\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) \quad \Delta H^\circ = -1936.8 \text{ kJ}$
 (3) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell) \quad \Delta H^\circ = -2219.2 \text{ kJ}$
37. Calculate the standard molar enthalpy of formation, ΔH_f° , for nickel tetracarbonyl, $\text{Ni}(\text{CO})_4(\text{g})$, given the following reaction:
- $$\text{Ni}(\text{s}) + 4\text{CO}(\text{g}) \rightarrow \text{Ni}(\text{CO})_4(\text{g}) + 159.6 \text{ kJ}$$
38. Calculate the standard enthalpy of reaction for the reaction as written:
- $$2\text{C}_2\text{H}_5\text{OH}(\ell) \rightarrow \text{C}_4\text{H}_6(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{H}_2(\text{g})$$
- ΔH_f° for $\text{C}_4\text{H}_6(\text{g}) = -391.1 \text{ kJ/mol}$ and refer to **Table 5.5**.
39. The table below shows the $\Delta H_{\text{comb}}^\circ$ for compounds that contain a chain of three carbon atoms. They differ in the number of $-\text{OH}$ groups attached to this chain of carbon atoms.

Standard Molar Enthalpies of Combustion, $\Delta H_{\text{comb}}^\circ$

| Name | Formula | $\Delta H_{\text{comb}}^\circ$ (kJ/mol) |
|----------------------|--|--|
| Propane | $\text{CH}_3\text{CH}_2\text{CH}_3(\text{g})$ | -2219 |
| 1-Propanol | $\text{CH}_2(\text{OH})\text{CHCH}_3(\ell)$ | -2021 |
| 1,2-Propylene glycol | $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_3(\ell)$ | -1828 |
| Glycerol | $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH})(\ell)$ | -1655 |

- a. Plot a graph of enthalpy of combustion, $\Delta H_{\text{comb}}^\circ$, vs. number of $-\text{OH}$ groups. Plot the vertical axis from 1000 kJ/mol to 2400 kJ/mol and the horizontal axis from zero $-\text{OH}$ groups to five $-\text{OH}$ groups.
 b. What trend in $\Delta H_{\text{comb}}^\circ$ is evident from this graph?
 c. The alcohol propylphycite, $(\text{C}_3\text{H}_4)(\text{OH})_4(\text{s})$, has been synthesized. Use your graph to predict $\Delta H_{\text{comb}}^\circ$ for this compound.

40. A mixture of ammonia, $\text{NH}_3(\text{g})$, and methane, $\text{CH}_4(\text{g})$, is burned in an excess of oxygen in a bomb calorimeter. The heat released during this combustion reaction is 1377.65 kJ. If the calorimeter has a heat capacity of 15.6 kJ/ $^\circ\text{C}$, by how much will the calorimeter and its contents change in temperature?
41. In a student investigation, a 1.20 g sample of zinc metal is added to a paper cup containing 90.00 mL of dilute hydrochloric acid, $\text{HCl}(\text{aq})$. The temperature of the solution increases from 22.44 $^\circ\text{C}$ to 24.65 $^\circ\text{C}$. Assume that the solution has the same specific heat capacity and density as water.
- Use this information to calculate the enthalpy of reaction, ΔH_r , per mole of zinc.
 - A reference text gives the enthalpy of reaction as -155 kJ/mol of zinc. Suggest one major reason for the difference in the experimental result and the reference value.
 - Calculate the efficiency of this experimental set-up to determine the standard molar enthalpy of reaction.
42. The equation below represents the burning of carbon disulfide, $\text{CS}_2(\ell)$, in a calorimeter. What mass of $\text{CS}_2(\ell)$ must have combusted to increase the temperature of 1.00 kg of water by 15.5 $^\circ\text{C}$?
- $$\text{CS}_2(\ell) + 3\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g}) + 1077 \text{ kJ}$$
43. The reaction written below shows the combustion of cyanogen, $\text{C}_2\text{N}_2(\text{g})$.
- $$\text{C}_2\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{N}_2(\text{g})$$
- $$\Delta H_r^\circ = -1096 \text{ kJ/mol}$$
- Calculate the enthalpy of formation of $\text{C}_2\text{N}_2(\text{g})$.
 - Write the thermochemical equation for the thermal decomposition of $\text{C}_2\text{N}_2(\text{g})$.
44. At constant pressure, a calorimetry experiment is to be set up to determine the enthalpy of reaction, in kilojoules per mole, when 250.0 mL of 0.500 mol/L $\text{HCl}(\text{aq})$ reacts with 50.0 mL of 1.0 mol/L $\text{NaOH}(\text{aq})$. In determining ΔH_r° , a student intends to base the calculation on the amount in moles of $\text{HCl}(\text{aq})$.
- After calculating the quantity of heat, Q , absorbed by the solutions, what step must be included in the calculation before determining the enthalpy of reaction using the equation $\Delta H_r = \frac{Q}{n}$?
 - If this step is not included, will the error lead to an answer that is too large or too small for ΔH_r ?
45. The temperature of 50.0 g of water changes from 28.5 $^\circ\text{C}$ to 26.9 $^\circ\text{C}$ when 1.00 g of ammonium bromide, $\text{NH}_4\text{Br}(\text{s})$, dissolves. What is the molar enthalpy of solution, $\Delta H_{\text{solution}}$, for this compound?
46. Fat has an energy content of 41.0 kJ/g. When a 0.68 g sample of fat is burned in a bomb calorimeter, the temperature of the calorimeter increases by 2.9 $^\circ\text{C}$. How efficient is the calorimeter at measuring the energy transfer if it has a rating of 8.7 kJ/ $^\circ\text{C}$?

Communication

47. The standard molar enthalpy of combustion of ethane, $\text{C}_2\text{H}_6(\text{g})$, is -1560.7 kJ/mol. Sketch an enthalpy diagram to summarize this information.
48. Your class is reviewing the main ideas about thermochemistry. You and your lab partner must demonstrate to the class the distinction between the terms heat and temperature. Suggest a simple demonstration to illustrate the difference in the terms to the class.

49. **BIG IDEAS** Technologies that transform energy can have societal and environmental costs and benefits. A manufacturing company currently uses coal as a fuel to heat its building. It is considering a switch to burning municipal waste as a fuel source. Examine the information available to the company regarding this new fuel source. Organize the data into a Plus, Minus, Interesting (PMI) chart to help decide if using municipal waste is a good decision.

Data Regarding New Fuel Source

- new equipment must be purchased and installed
- estimated energy content from coal is 26 kJ/g
- unknown costs to monitor emissions
- cost saving over using coal, since a municipality wants to get rid of this product
- estimation that $\text{CO}_2(\text{g})$ emission would be reduced 30% compared with coal
- health risk of using a fuel containing plastics including polyvinyl chlorides (PVCs)
- waste is not of uniform and consistent energy content
- company will be seen as environmentally friendly, leading to potential increased sales of their product
- diversion of waste from landfill sites
- estimated energy content from current waste is 13 kJ/g

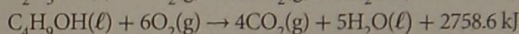
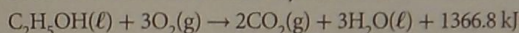
50. You have a product that you want to market as a portable food warmer for use by campers. You plan to prepare an advertisement that can be used for a print medium such as a newspaper or for use on a Web site for potential customers to read. What main points would you stress to make this an appealing product?
51. On an outdoor winter class trip, your teacher cautions against using snow as a source of drinking water. Your friend says that this is only common sense because there is no way of knowing what unhealthy material could be mixed in with the snow. What thermochemical reason can you give as another explanation for the teacher's instruction?
52. From an environmental point of view, hydrogen gas is an ideal fuel because the product of its combustion is water. A great deal of energy is needed to extract $\text{H}_2(\text{g})$ from water by electrolysis, the process of passing a direct electric current through water.
 - a. Research some of the ways in which technology is trying to develop the potential of hydrogen energy.
 - b. Use a fishbone diagram graphic organizer to organize and present the pros and cons of using hydrogen as a fuel source. Refer to Appendix A for a model of a fishbone diagram.
53. You are a chemist in a power plant that produces nuclear energy. You are invited to speak to members of a local service club in the city where you live.
 - a. Outline some of the points you would make to the group that would emphasize the positive aspects of this energy source while minimizing the negative aspects.
 - b. Refer to Appendix A for a description of graphic organizers. Select one of the graphic organizers and organize the information for your presentation as a handout.
54. Transportation and heating top the list of ways in which people depend on fossil fuels.
 - a. For your family, think of the ways that fossil fuels have been used to make what you use on a daily basis. Consult other family members, if possible, for their input. Select a graphic organizer from Appendix A to help you form a "picture" of how fossil fuels are part of daily living.
 - b. Use a pie chart to compare your family's dependency on fossil fuels in four areas: transportation, heating, electricity, and a fourth area, "other products."
55. Select a graphic organizer from Appendix A to outline the questions that could be asked when considering the characteristics of a fuel.
56. There is a significant difference in the temperature of beach sand and that of the nearby water on a hot sunny day. This difference in temperature is less noticeable on a hot cloudy day.

Demonstrate your knowledge of thermochemistry using the terms *specific heat capacity* and the *first and second laws of thermodynamics*, as well as the expression for calculating the quantity of heat, Q , to explain these observations to a friend.
57. A reporter is preparing to write a feature article on alternative energy sources that could reduce dependency on fossil fuels. The plan is to interview business people in the community who are directly involved with the development and distribution of energy sources.
 - a. Make a list of 10 questions that the reporter might prepare before interviewing these people.
 - b. Assume that you are a business person who advocates the use of geothermal energy to heat a home. Research this energy source and respond to the questions that the reporter plans to ask.
58. Summarize your learning in this chapter using a graphic organizer. To help you, the Chapter 5 Summary lists the Key Terms and Key Concepts. Refer to Using Graphic Organizers in Appendix A to help you decide which graphic organizer to use.

Application

59. Refer to the standard enthalpy of formation data given in Appendix B. Which of the three oxides of iron that are listed is the most thermally stable? Give a reason for your answer.
60. Both methane, $\text{CH}_4(\text{g})$, and hydrogen gas, $\text{H}_2(\text{g})$, are effective fuels. Their thermal energy can be expressed in energy units per unit of mass or per unit of volume. Use the equations as written below to compare these fuels in terms of available energy in
 - a. kilojoules per gram.
 - b. kilojoules per litre.
$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + 890.8 \text{ kJ}$$
$$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell) + 285.8 \text{ kJ}$$

61. Determine the energy of combustion, in kilojoules per gram, for an alcohol burner containing 30% butan-1-ol and 70% ethanol by mass.



62. **BIG IDEAS** Energy changes and rates of chemical reactions can be described quantitatively. From the first law of thermodynamics, you know that in a chemical reaction energy is conserved but can be converted from one form to another. For example, a microwave oven uses electrical energy to emit microwaves of a frequency that specifically is absorbed by and heats only water. A microwave oven uses electrical energy at a rate of $1.100 \times 10^3 \text{ J/s}$ for 2.00 min. The oven converts this electrical energy to microwaves with an efficiency of 81.02%. The efficiency with which 500.0 g of water in a Pyrex™ bowl inside the oven absorbs the microwaves is 98.3%.

- What is the expected temperature change of the water?
- Suggest an explanation as to why the observed temperature change was 42.6°C.
- Suggest reasons why the electrical energy is not converted completely to microwaves.

63. A calorimetry experiment is set up to determine the enthalpy of solution, $\Delta H^\circ_{\text{solution}}$. The following occurs:

- 4.10 g of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2(\text{s})$, is dissolved in 100.0 mL of water in a double-insulated coffee cup calorimeter.
- The temperature of the water increases from 19.6°C to 21.1°C.
- For the calculations, it is assumed that for the solution formed, the specific heat capacity is $4.19 \text{ J/g}\cdot^\circ\text{C}$ and the density is 1.0 g/mL .

For each description given below, explain whether the calculated $\Delta H^\circ_{\text{solution}}$ will be larger or smaller than the theoretical value.

- After adding the $\text{NaC}_2\text{H}_3\text{O}_2(\text{s})$, the solution was stirred once and left standing during the dissolving process.
- The initial temperature was incorrectly recorded as 16.9°C.
- The actual specific heat capacity and the density of the solution are both slightly greater than the values accepted for water.

64. Which would give more accurate results for the determination of an enthalpy of combustion reaction: a bomb calorimeter using a constant volume system or a flame calorimeter using a constant pressure system? Explain your reasoning in a few sentences.

65. In an article on the Internet, you read the statement, “27 m³ of natural gas is equivalent to a gigajoule (GJ) of energy.” Realizing that many Internet sources are not reliable, you are skeptical and want to verify it. Decide what information you need, research it, and determine whether the statement is accurate.

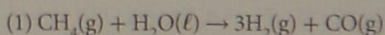
66. A thermal generating station is phasing out the use of coal and converting to the use of biomass pellets. What are some pros and cons of this change?

67. **BIG IDEAS** Technologies that transform energy can have societal and environmental costs and benefits. Hybrid cars have been called “the car of the future.” They have two engines: a traditional gasoline engine, and an electric motor and batteries. Research the topic of hybrid vehicles and report on the advantages and disadvantages from an environmental and economic perspective.

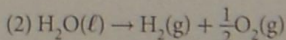
68. Your task is to determine the thermal heat content in a food product by carrying out a combustion of the food in a bomb calorimeter. Before combustion, you oven-dried the food. Why would this step be important in order to obtain accurate results?

69. **BIG IDEAS** Technologies that transform energy can have societal and environmental costs and benefits. Controversy continues over the construction of wind turbines at various locations on the shores of the Great Lakes in Ontario. Research this topic and be prepared to present arguments for and against the development of this energy source.

70. Hydrogen gas is a very environmentally friendly fuel source. One factor that is important in determining whether it is used as a fuel source is the cost of production. Use the two equations below to evaluate which reaction requires more energy to produce 1 mol of $\text{H}_2(\text{g})$. Reaction (1) as written produces $\text{H}_2(\text{g})$ from methane and is 80.5% efficient. The production of $\text{H}_2(\text{g})$ by electrolysis of water, as shown in reaction (2), is 49.1% efficient.



$$\Delta H^\circ_r = +205.9 \text{ kJ}$$



$$\Delta H^\circ_r = +285.8 \text{ kJ}$$

Select the letter of the best answer below.

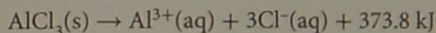
- K/U** Which one of the following gases is considered a greenhouse gas and a major contributor to global warming?
 - hydrogen chloride
 - sulfur dioxide
 - hydrogen
 - carbon dioxide
 - nitrogen
- K/U** Which one of the following has a non-zero value for enthalpy of formation?
 - $\text{N}_2(\text{g})$
 - $\text{Ne}(\text{g})$
 - $\text{Na}^+(\text{aq})$
 - $\text{Cl}_2(\text{g})$
 - $\text{He}(\text{g})$
- K/U** Which equation represents the formation of $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$?
 - $17\text{C}(\text{s}) + \frac{35}{2}\text{H}_2(\text{g}) + \text{O}_2(\text{g}) + \text{Ca}(\text{s}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$
 - $18\text{C}(\text{s}) + 35\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) + \text{Ca}(\text{s}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$
 - $34\text{C}(\text{s}) + 2\text{O}_2(\text{g}) + 2\text{O}_2(\text{g}) + \text{Ca}(\text{s}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$
 - $36\text{C}(\text{s}) + 35\text{H}_2(\text{g}) + 2\text{O}_2(\text{g}) + \text{Ca}(\text{s}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$
 - $18\text{C}(\text{s}) + 17\text{H}(\text{g}) + \text{O}_2(\text{g}) + \text{Ca}(\text{s}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s})$
- T/I** What amount of heat must be removed from 10.0 g of water at 1.00°C so that the water reaches the freezing point (but does not freeze)?
 - 0.419 J
 - 41.9 J
 - 0.00419 J
 - 419 J
 - 4190 J
- T/I** When a 2.00 g sample of a substance is combusted in a bomb calorimeter that has a heat capacity of $2.337\text{ kJ}/^\circ\text{C}$, the temperature increases by 3.03°C . How much heat was released during the combustion?
 - 6.06 kJ
 - 7.08 kJ
 - 14.2 kJ
 - 0.771 kJ
 - 3.54 kJ
- T/I** What is the efficiency of a system in which 200.0 g of water absorbs 40.0 kJ of thermal energy from a heater that emits 50.0 kJ of heat?
 - 40.0%
 - 90.0%
 - 80.0%
 - 180.0%
 - 12.5%
- K/U** In which one of the following situations does the greatest absorption of thermal energy occur?
 - 10.0 g of water freezes
 - 10.0 g of ice melts
 - 10.0 g of water vapour condenses
 - 10.0 g of water evaporates
 - 10.0 g of water heats up by 10.0°C
- T/I** Determine the value of ΔH° for the reaction $2\text{C} + \text{B} \rightarrow \text{BC}_2$, given the following information:
 - $\text{AC}_2 \rightarrow \text{A} + 2\text{C} \quad \Delta H^\circ = +50\text{ kJ}$
 - $\text{AC}_2 + \text{B} \rightarrow \text{BC}_2 + \text{A} \quad \Delta H^\circ = -20\text{ kJ}$
 - 70 kJ
 - 30 kJ
 - +20 kJ
 - 50 kJ
 - +30 kJ
- K/U** You have a sample of water at 65°C . When it is warmed to a temperature of 125°C at standard pressure, how has the energy of the water changed?
 - Only potential energy increases.
 - Only kinetic energy increases.
 - Potential energy remains the same and kinetic energy increases.
 - Potential energy increases and kinetic energy stays the same.
 - Both potential energy and kinetic energy increase.
- T/I** Given the reaction below, how much thermal energy is required to decompose 123.9 g of $\text{Ag}_2\text{S}(\text{s})$?

$$2\text{Ag}(\text{s}) + \text{S}(\text{s}) \rightarrow \text{Ag}_2\text{S} + 31.8\text{ kJ}$$
 - 15.9 kJ
 - 63.6 kJ
 - 31.8 kJ
 - 7.95 kJ
 - 42.7 kJ

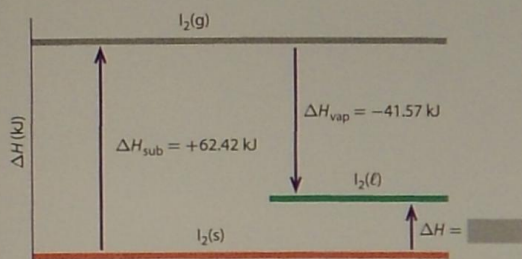
Use sentences and diagrams as appropriate to answer the questions below.

- K/U** You have two samples of water, one at 25°C and another at 40°C . What does this information tell you about the energy of the particles and the total energy of the samples?
- K/U** Although heating and transportation are the major uses of fossil fuels, it has been estimated that almost 5% of the air pollution in Canada is produced by the use of electric or gas-powered garden and lawn equipment. List some items used for home lawn and garden work and suggest ways in which the items could be modified to have less impact on the environment.
- T/I** How much energy can be recovered by a condensing furnace that is 97% efficient, from the combustion of natural gas that contains $2.0 \times 10^6\text{ g}$ of methane?

14. **A** When 6.85 g of aluminum chloride, $\text{AlCl}_3(\text{s})$, is dissolved in 255.0 mL of water, the final temperature of the solution is 48.7°C . What was the initial temperature of the water?



15. **T/I** The enthalpy diagram below shows the relative potential energy of iodine in each of its three states. Write the thermochemical equation for the process indicated by the grey box.



16. **A** Refer to the table of standard molar enthalpies of formation in Appendix B to determine the enthalpy of reaction, ΔH_r° , for calcium carbide, $\text{CaC}_2(\text{s})$, and water. $\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + \text{Ca}(\text{OH})_2(\text{s}) + 128.0 \text{ kJ}$
17. **A** For the following reaction
 $\text{HNO}_3(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{KNO}_3(\text{aq}) + 55.31 \text{ kJ}$
 when 400.0 mL of 0.0500 mol/L $\text{HNO}_3(\text{aq})$ is added to an unknown volume of 0.0500 mol/L $\text{KOH}(\text{aq})$, the temperature increases from 18.67°C to 19.00°C . Assuming that both solutions have a specific heat capacity of $4.19 \text{ J/g}\cdot^\circ\text{C}$ and a density of 1.000 g/mL , what volume of $\text{KOH}(\text{aq})$ was used?
18. **T/I** Use the equations below to determine the enthalpy of reaction, ΔH_r° , for
 $2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_5(\text{g})$
 (1) $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 3\text{O}_2(\text{g}) \quad \Delta H^\circ = +447.4 \text{ kJ}$
 (2) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H^\circ = -114.2 \text{ kJ}$
19. **C** On a calm winter day, it begins to snow and the air temperature increases. Explain this increase based on thermodynamics at a level that could be understood by a younger sibling interested in chemistry.
20. **C** When propane, $\text{C}_3\text{H}_8(\text{g})$, undergoes complete combustion to $\text{CO}_2(\text{g})$ and gaseous water, $\text{H}_2\text{O}(\text{g})$, the enthalpy of combustion, $\Delta H_{\text{comb}}^\circ$, is -2043.9 kJ/mol . With a partner, discuss whether the value of $\Delta H_{\text{comb}}^\circ$ would change if the product was liquid water, $\text{H}_2\text{O}(\text{l})$.
21. **T/I** How much heat must a stove burner release in order to raise the temperature of 1.245 kg of water from 24°C to the boiling point, if the water is in a pot on the stove? Assume that the transfer of the heat from the burner to the water is 34.5% efficient.
22. **A** A bomb calorimeter has a heat capacity of $5923 \text{ J/}^\circ\text{C}$. When a 0.7450 g sample of fat is burned, the temperature increases from 18.45°C to 22.62°C .
 a. What is the enthalpy of combustion, in kilojoules per gram, for this sample of fat?
 b. It is estimated that 9.48% of the energy in this sample of fat is used in digestion. How much of the energy in this fat will be available as heat and as energy for muscle activity?
23. **A** What mass of propane would have to be burned to heat a 5.0 kg iron barbecue from 25°C to 190°C if the heat transfer is 45% efficient? The specific heat capacity of iron is $0.46 \text{ J/g}\cdot^\circ\text{C}$.
24. **T/I** Refer to the standard molar enthalpies of formation in Appendix B and determine whether it is the reactants or the products in the reaction below that have more potential energy.
 $4\text{FeS}_2(\text{s}) + 11\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 8\text{SO}_2(\text{g})$
25. **C** Develop a step-by-step procedure for comparing the standard molar enthalpies of combustion of alkanes with their corresponding alkenes having one double bond and the same number of carbon atoms. Include the following:
 • all of the data required and a description of how the data is used for the comparison
 • a flowchart that could act as a guide for the comparison
 • a description of how a graph could be used to display comparisons for compounds with two to ten carbon atoms

Self-Check

| If you missed question ... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 |
|----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Review section(s)... | 5.4 | 5.2 | 5.2 | 5.2 | 5.2 | 5.4 | 5.2 | 5.3 | 5.1 | 5.2 | 5.1 | 5.4 | 5.2 | 5.1 | 5.3 | 5.2 | 5.3 | 5.1 | 5.3 | 5.2 | 5.2 | 5.2 | 5.3 | 5.3 | 5.3 |